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October 1998

PROCEEDINGS:

LOW- AND NO-VOC COATING TECHNOLOGIES: 2ND BIENNIAL INTERNATIONAL CONFERENCE

March 13-15, 1995
Durham, North Carolina

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16. ABSTRACT The report documents an international conference that provided a forum for the exchange of technical information on coating technologies. It focused on improved and emerging technologies that result in fewer volatile organic compound (VOC) and toxic air emissions than those from traditional coatings. EPA's National Risk Management Research Laboratory and Research Triangle Institure cosponsored the conference, entitled, "Low- and No-VOC Coating Technologies: 2nd Biennial International Conference." It was held on March 13-15, 1995, in Durham, NC. Approximately 175 people participated. Plenary presentations provided perspectives from the coatings industry and from federal and state government representatives. Technical papers described new coating technologies, coating application equipment, chemical agents for Coatings removal, and issues associated with measuring the VOC content of coatings. The technical papers presented at the conference focused on regulations, radiation-curable coatings, life cycle analysis of coatings, surface preparation, powder coatings, automotive applications, wood furniture technologies, military applications, architectural and industrial maintenance coatings, and other low- and no-VOC coating technologies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Emission	Pollution Prevention	13B	14G
Coatings	Automotive Industry	Stationary Sources	11C	05C, 13F
Coating Processes	Latex	Wood Furniture	13H	11J
Organic Compounds	Powder	Volatile Organic Compounds (VOCs)	07C	
Volatility	Wood		20M	11L
Toxicity	Furniture	Industrial Coatings	06T	15E
Military Research	Architecture		14F	13M, 05F

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

The report documents an international conference that provided a forum for the exchange of technical information on coating technologies. It focused on improved and emerging technologies that result in fewer volatile organic compound (VOC) and toxic air emissions than those from traditional coatings. Among the new products and improvements discussed were a 100%-solids liquid sprayable coating, solventless architectural coatings, use of effervescent spray technology to eliminate volatile diluents, and the use of life cycle assessment to develop an environmental labeling scheme for coatings. It also includes an examination of VOC emissions to the indoor air environment from latex paints.

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INTRODUCTION

In 1992, surface coating operations accounted for approximately 24 percent of all volatile organic compound (VOCs) released from industrial processes[1]. While pollution control equipment can reduce solvent emissions from some coating operations, adoption of pollution prevention techniques such as the use of lower-emitting coatings, in many cases provides a cost-effective alternative. For many coatings applications, such as small coating operations or architectural and industrial maintenance applications, pollution prevention may be the only economically viable approach to reducing emissions. Lower-emitting coating technologies are being developed rapidly to reduce VOC and hazardous air pollutants (HAP) emissions from coating operations in a wide variety of industrial and commercial applications. These technologies include higher solids solventborne coatings, waterborne coatings, coatings containing reactive diluents, 100 percent solids liquid sprayable coatings, powder coatings, radiation curable coatings, and spray coatings that employ supercritical carbon dioxide as a solvent. In addition to new coating technologies, improvements in coating application equipment and application techniques continue to offer opportunities for substantial reductions in VOC emissions through improved application efficiency.

A conference entitled "Low- and No-VOC Coating Technologies: 2nd Biennial International Conference" was held on March 13 -15, 1995, in Durham, North Carolina. The primary purpose of the conference was to provide a forum for the exchange of technical information on lower-emitting coating technologies. Plenary presentations provided perspectives on new technology needs and developments from the coatings industry and from federal and state government representatives. Papers described some of the latest developments in new coating technology, coating application equipment, chemical agents for coating removal, and issues associated with measuring the VOC content of coatings.

Approximately 175 people participated in the conference. Of these attendees, approximately 13 percent were coating users, 12 percent were environmental consultants, 49 percent were government agency representatives, 9 percent were coating manufacturers, 3 percent were in coating marketing and sales, 3 percent were educators, and 11 percent were in other categories. There were six foreign participants: two from Canada, two from Belgium, one from Italy, and one from the United Kingdom.

Technical papers presented at the conference focused on regulations, radiation curable coatings, life-cycle analysis of coatings, surface preparation, powder coatings, automotive applications, wood furniture technologies, military applications, architectural and industrial maintenance coatings, and other low- and no-VOC coating technologies. Paper topics included a description of a 100%- solids liquid sprayable coating, solventless architectural coatings, use of effervescent spray technology to eliminate volatile diluents, the use of lifecycle assessment to develop an environmental labeling scheme for coatings, and an examination of VOC emissions to the indoor air environment from latex paints.

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[1]Nizich, Sharon, 1993. National Air Pollutant Emission Trends, 1900-1992. EPA-454/R-93-032 (NTIS PB94-152097). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. October.

SESSION 1

OPENING

WELCOME ADDRESS

by

Frank Princiotta

Director

U.S. Environmental Protection Agency

National Risk Management Research Laboratory

Air Pollution Prevention and Control Division

Research Triangle Park, North Carolina

KEYNOTE

by

Alexander Ramig, Jr.

Vice President of Research and Development

ICI/GLIDDEN

Strongsville, Ohio

"State Perspective" (Paper not available for publication.)

by

Gary Hunt

North Carolina Office of Waste Reduction

Raleigh, North Carolina

"University Perspective"

by

John Massingill

Coatings Research Institute

Ypsilanti, Michigan

"EPA Coatings Research"

by

Michael Kosusko

U.S. Environmental Protection Agency

National Risk Management Research Laboratory

Air Pollution Prevention and Control Division

Research Triangle Park, North Carolina

WELCOME

Frank T. Princiotta

Director

Air and Energy Engineering Research Laboratory*

(*) In mid-1995, redesignated the Air Pollution Prevention and Control Division of EPA's National Risk Management Research Laboratory.

WELCOME TO

THE RESEARCH TRIANGLE PARK,

DURHAM, and

THE LOW- AND NO-VOC COATING TECHNOLOGIES: 2ND BIENNIAL INTERNATIONAL CONFERENCE

CONFERENCE GOALS

- EXCHANGE TECHNICAL INFORMATION ON INNOVATIVE COATING TECHNOLOGIES
- ESTABLISH AND/OR REINFORCE COOPERATIVE RELATIONSHIPS
- PRESENT RESULTS OF AEERL COATINGS RESEARCH (12 of 46 Topics)

THE AIR AND ENERGY ENGINEERING RESEARCH LABORATORY (AEERL)

ENVIRONMENTAL MISSION

- DEVELOP TECHNOLOGIES TO REDUCE AIR POLLUTION BY:
  - Pollution Prevention
  - End-of-Pipe Control
- ENHANCE COMPETITIVENESS OF U.S. BUSINESSES BY IDENTIFYING TECHNOLOGIES THAT ARE:
  - Practical and
  - Cost-Effective

THE AIR AND ENERGY ENGINEERING RESEARCH LABORATORY (AEERL)

RELATIONSHIP TO REGULATORY DEVELOPMENT

- ORGANIZATIONALLY, AEERL IS NOT RELATED TO THE PROGRAM OFFICES UNTIL THE ADMINISTRATOR'S LEVEL
- AEERL'S FOCUS IS RESEARCH OF INNOVATIVE TECHNOLOGIES
- HOWEVER, REGULATORY SUPPORT IS PART OF OUR MISSION

THE AIR AND ENERGY ENGINEERING RESEARCH LABORATORY (AEERL)

POLLUTION PREVENTION RESEARCH

- SURFACE COATING AND SOLVENT CLEANING (Organic Chemicals)
- INDOOR AIR QUALITY (Household and Office Emissions)
- STRATOSPHERIC OZONE DEPLETION (CFC and Halon Replacements)
- GLOBAL WARMING (Energy Issues)

ICI Paints

Glidden

RESPONSIBLE ENVIRONMENTAL STEWARDSHIP IMPROVED COATING TECHNOLOGIES RESULT IN NO OR LESS VOC AND TOXIC AIR EMISSIONS

Summary of Paper presented by Dr. Alexander Ramig, Jr., Director-International Research & Development, ICI Paints

Waterborne technology

ICI Paints worldwide has been in the forefront of waterborne technology for almost half a century. Application of this technology can be found in each of its core businesses: decorative paints, coatings for food and beverage cans and autobody refinishes.

Our main focus of research and development is on low- or no-VOC product, safety, cost of production and benefits for end users. In 1948, The Glidden Company, a member of ICI Paints, developed the first waterborne latex paint, removing 90% of petroleum solvent from consumer interior paint. Two years later, Glidden introduced the first successful application of waterborne technology to the industrial finishing market in automotive primers and in acoustical tiles.

In 1960, the company introduced electrocoating to finishers of automotive parts, home appliances and other metal products, as well as waterborne coatings for industrial maintenance. In 1970, Glidden developed powder coatings which are environmentally clean when baked on major metal parts in the manufacture of home appliances, outdoor furniture, trucks, vans and many other metal items.

In 1976, the company developed and marketed the first waterborne can lining to protect flavor and taste of beer and soft drinks.

In 1992, ICI Paints introduced the first no-VOC consumer paint by removing the remaining petroleum-based solvent from latex paint, using new paint technology. ICI's autobody refinish coatings include a waterborne refinish system for autobody repair, which was introduced in 1993.

Industry-Government Relationships

Improvement in industry-government relationships is sought through seeking out true partnerships, recognizing obstacles and eliminating self-serving objectives both by government agencies and industries. The purpose of industry is to service customers and create shareholder value; that of the government is to serve the people in the national interest without being burdensome. A bureaucratic structure

/more

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

in either industry or government leads to duplication, waste, costly decisions, confusion, self-serving departments and loss of its founding purpose.

Industry and government can seek out true partnerships by agreeing on common goals and by conceiving, developing, monitoring and funding projects jointly. Together they can create and manage a strategically balanced portfolio of projects to create value and enhance American industry's worldwide competitive position and serve the national interest as well.

VOC Emissions

In the area of VOC emissions across the United States from cities (about 100) that had higher than acceptable ozone levels, EPA reports that 47% is generated by highway vehicles, 15% by organic solvent evaporation, 9% by surface coatings and 12% split between the petroleum and gas marketing industries; 5% by treatment, storage and disposal facilities; 4% by other industry; and chemical manufacturing, solid waste disposal, fuel combustion, non-residential and miscellaneous each share 1% in emission measurement.

The author and his company support a national VOC rule with key issues centered on uniformity and simplicity. These include:

- emphasis on regulation to be acceptable to states so that they will not be tempted to simplify each in their own way

- application to attainment as well as non-attainment coatings areas

- Use of a series of VOC Tables as a means to restrict VOC limits, as opposed to other schemes such as "Corporate Average - CAVE," etc.

- Promotion of specific categories (as opposed to general) that can be narrowly defined in order to simplify compliance and ensure strict enforcement - "button up the loopholes"

- Limitation on administrative requirements, such as labeling, reporting and recordkeeping, using procedures typified by current state regulations

- Support of a fee criteria that is simple and rewards companies that strive to produce low-VOC product

end 9/12/95

COATINGS RESEARCH INSTITUTE

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

JOHN MASSINGILL
DIRECTOR

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NSF COATINGS RESEARCH CENTER PARTNERS

- EASTERN MICHIGAN UNIVERSITY
- MICHIGAN MOLECULAR INSTITUTE

NSF COATINGS RESEARCH CENTER MISSION

- To be a leading academic organization that develops relevant scientific knowledge
- For understanding and expanding the technology of paints and coatings
- For the benefit of its members and
- To enlarge the cadre of scientists and technologists capable of working effectively with coatings

Institute Objective

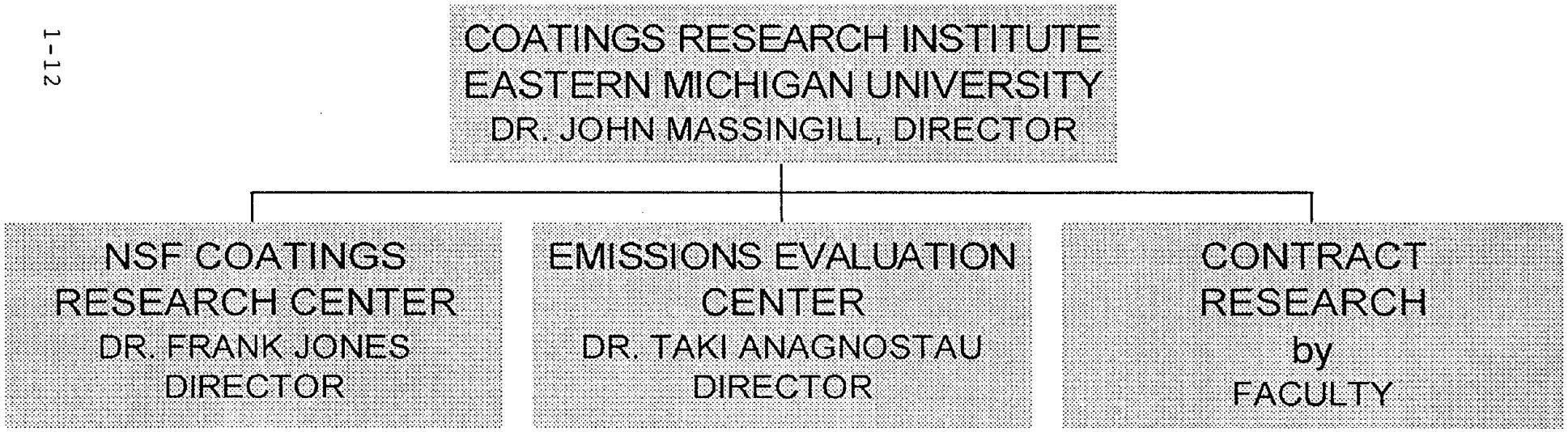
- PROVIDE SCIENTIFIC KNOWLEDGE FOR UNDERSTANDING THE TECHNOLOGY OF PAINTS

- HELP INDUSTRY MEET GOVERNMENT MANDATES

- DEVELOP COATING SCIENTISTS

Meeting the Needs

- ORGANIZATION



NSF COATINGS CENTER

DR. FRANK JONES

DIRECTOR

NSF COATINGS RESEARCH CENTER

- BENEFITS TO MEMBERS
  - INFLUENCE CENTER STRATEGY
  - INFLUENCE PROJECT SELECTION
  - DEVELOP RESEARCH PORTFOLIO
  - RAPID INFOMATION TRANSFER
  - MEET UNIVIVERSITY RESEARCHERS
  - INFORMAL CONSULTING
  - PREFERENTIAL ACCESS TO PATENTS
  - MEET POTENTIAL EMPLOYEES

NSF COATINGS RESEARCH CENTER OBJECTIVES

- BACKGROUND
  - Anticipated regulation of voc, hap, odor, safety, and waste will require revolutionary changes in coatings technology
  - Coatings industry will be required to change resins, formulas, and application methods

NSF COATINGS CENTER OBJECTIVES

- CORE COMPETENCIES
  - NEW CONCEPTS IN POLYMER SYNTHESIS AND CROSSLINKING
  - PRINCIPLES OF PHYSICAL PHENOMENA CRITICAL TO COATINGS
  - CHARACTERIZATION METHODS FOR COATINGS

NSF COATINGS RESEARCH CENTER MEMBERS

- AKZO NOBEL
- DOW CHEMICAL
- FLINT INK
- FORD MOTOR
- ICI-GLIDDEN
- PPG INDUSTRIES
- PRA LABS
- RHONE-POULENC
- SOUTH COAST AQMD
- STATE OF MICHIGAN

Cost Analysis

- $30,000 PER YEAR
- GET INFORMATION OF VALUE TO MEMBER
- INTELLECTUAL PROPERTY
- PATENT RIGHTS
- POTENTIAL EMPLOYEES

NSF Coatings Research Center
Our Strengths

- CROSS-LINKING CHEMISTRY
- CROSS-LINKED FILM PROPERTIES
- RHEOLOGY CONTROL
- SCANNING PROBE MICROSCOPY
- LOW VOC AND NO VOC COATINGS
- CORROSION PROTECTION
- SURFACE SCIENCE AND ADHESION

NSF COATINGS RESEARCH CENTER TANGIBLE ACCOMPLISHMENTS

- MEMBER COMPANIES STARTED 6 PROJECTS @ $80,000 EACH TO EXPLOIT CENTER RESULTS
- 26 PUBLICATIONS AND PRESENTATIONS
- 7 INVENTION DISCLOSURES
- 3 PATENT APPLICATIONS
- ONE SMALL BUSINESS SPIN-OFF
- 20 STUDENTS IN COATINGS RESEARCH

EMISSIONS EVALUATION CENTER

DR. TAKI ANAGNOSTOU
DIRECTOR

EMISSIONS EVALUATION CENTER

- GOAL
  - DEVELOPMENT OF RELIABLE ODOR DETECTION PROCEDURES FOR THE COATINGS INDUSTRY
  - GUIDE RE-FORMULATION TO MINIMIZE PLANT ODORS IN COMMUNITY

EMISSIONS EVALUATION CENTER

- RESULTS
  - THE AUTO INDUSTRY HAS USED THE EEC RESULTS TO REDUCE ODOR EMISSIONS FROM PRODUCTION SITES
  - ONE MEMBER HAS INCREASED SALES DRAMATICALLY AS A DIRECT RESULT OF CENTER WORK

CONTRACT RESEARCH

CONTRACT RESEARCH BY FACULTY

- CURRENT CONTRACT RESEARCH
  - WATER-BORNE COATINGS
  - 100% SOLIDS COATINGS
  - MAR RESISTANT AUTO COATINGS
  - NON-ISOCYANATE TOP COATS
  - RESINS FROM RENEWABLE RESOURCES
  - REACTIVE DILUENTS FOR LOW VOC ALKYDS

CONTRACT RESEARCH BY FACULTY

- RESULTS
  - LIQUID CRYSTAL POLYMERS IN COATINGS
    - » 5 US PATENTS, 4 PENDING
    - » PILOT SCALE PRODUCTION
  - MONSANTO PROJECT
    - » NEW INSIGHTS INTO MELAMINE RESIN CURE
    - » DISCOVERY OF LOW TEMPERATURE CURE MELAMINE CROSSLINKERS
  - RESIN DILUENT PROJECT
    - » REDUCED VOC BY REACTIVE DILUENT
    - » DEMONSTRATION PROJECT SCHEDULED 1995

REACTIVE DILUENTS FOR ALKYD COATINGS

STEP 1

IDEA: REACTIVE DILUENTS FOR COATINGS

FINANCIAL SUPPORT:
USAID, USDA, SCAQMD,EPA, SCE

STEP 2

INTERMEDIATE DEVELOPMENT:
PRA LABORATORIES, INC.

FINANCIAL SUPPORT:
EPA, SCAQMD
TECHNICAL ADVISORY TEAM
INDUSTRIAL MEMBER TO TEST

Next Steps

- JOIN THE NSF CENTER
  - TO SHARE IN NEW TECHNOLOGY
- JOIN THE EEC
  - TO CONTROL ODOR IN YOUR PLANTS
- CONTRACT RESEARCH
  - TO SOLVE YOUR PROBLEMS

FOR FURTHER INFORMATION

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

EPA Coatings Research

by

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Prepared for:

Low- and No-VOC Coating Technologies:
2nd Biennial International Conference
Durham, North Carolina
March 13, 1995

I. INTRODUCTION

"For more than two decades, the U.S. Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory (AEERL)[a], located in Research Triangle Park, North Carolina, has been exploring control approaches for the pollutants and sources that contribute to air quality problems. For example, AEERL has successfully developed and demonstrated cost-effective sulfur dioxide, nitrogen oxides (NO_x), and particulate control technologies for fossil fuel combustion sources. More recently, it has expanded its interest to areas that include organics control, indoor air quality, radon, stratospheric ozone depletion, and global warming. AEERL also develops inventories of many types of air emissions. Over the past several years, AEERL has made a substantial effort to expand pollution prevention as the preferred choice to reduce air emissions. Its goal is to conduct research that will result in the greatest possible reduction of air pollution for the lowest cost[1]."

The Organics Control Branch (OCB)[b] of AEERL is charged with developing and assessing pollution prevention (P^2) techniques for reducing emissions of organic compounds to air, *i.e.*, volatile organic compounds (VOCs) and hazardous air pollutants (HAPs or air toxics). This presentation provides a brief overview of OCB's P^2 research on surface coating technologies.

In recent years, HAPs and VOCs have been recognized as contributors to human health problems internationally. EPA's report, Unfinished Business, grouped these pollutants into one category entitled "hazardous/toxic air pollutants" and identified this category as one of the highest risks for causing excess cancer deaths[2]. In addition to direct effects, VOCs react in the atmosphere to form ozone (and other oxidants) which also affect health, as well as cause damage to materials, crops, and forests. Even though the EPA has established an ambient ozone standard of 120 parts per billion (ppb), millions of people live in areas in the U.S. where the ozone standard is routinely exceeded[c]. The combination of VOC-produced ozone and human exposures to HAPs makes organic emissions one of the most pressing environmental problems we face.

II. RESEARCH AND DEVELOPMENT STRATEGY

OCB's overall strategy for answering this question and moving ahead with research and development (R&D) is as follows:

Step 1. Determine the important organics responsible for:
(1) Tropospheric ozone;

---

[a]The Air and Energy Engineering Research Laboratory (AEERL) was renamed during the EPA Office of Research and Development's (ORD's) reorganization during mid-1995. It is now the Air Pollution Prevention and Control Division (APPCD) of the National Risk Management Research Laboratory (NRMRL).

[b]The functions of the Organics Control Branch (OCB) were assumed by the newly formed Emissions Characterization and Prevention Branch (ECPB) during the mid-1995 ORD reorganization.

[c]In November 1996, EPA proposed to change the ambient ozone standard to 80 ppb averaged over an 8 hour period.

(2) Non-cancer toxicity; and
(3) Cancer.

Step 2. Determine the important sources of these organics.

Step 3. Obtain information on the important sources so that P^2 opportunities can be developed and evaluated.

Step 4. Conduct P^2 research.

A. Compounds.

This involved a screening approach which used: (1) the 1985 NAPAP (National Acid Precipitation Assessment Program)-speciated VOC inventory to identify the most important compounds contributing to ozone and (2) the 1991 TRIS (Toxics Release Inventory System) inventory to identify the most important toxic compounds contributing to ozone, non-cancer toxicity, and cancer[3,4]. Emissions were weighted according to ozone creation potential, toxic effects potential, and unit cancer risk to identify the most important compounds and sources. The problem endpoints and the weighting factors used are indicated in Table I.

Table I. Health Risk Weighting Factors.

PROBLEM ENDPOINT	WEIGHTING FACTOR
Ozone	Incremental ozone reactivity
Non-cancer toxicity	Lowest observable adverse effects level (LOAEL)
Cancer	Cancer inhalation unit risk values

The most important compounds and sources causing ozone, non-cancer toxicity, and cancer are subdivided by the type of environmental concern as shown in Tables II, III, and IV.

B. Industries

Research areas (pollutants, processes, and sources) have been identified for which AEERL/OCB can provide the maximum beneficial environmental impacts, taking into account technical, resource, regulatory, and political needs. Prevention approaches which are efficient and cost-effective will be identified, assessed, and demonstrated with the active participation of industry, small businesses, and other government agencies. Present and near-future strategic directions will include emphasis on the reduction of the emissions of "high-priority" organic compounds from a few key manufacturing industries.

Table II. Key Compounds Contributing to Ozone.

OZONE
Ethylene
Substituted benzenes
Xylenes
C_7 & > alkanes
C_4 - C_6 alkanes
C_4 - C_7 olefins
1,3-Butadiene

Table III. Key Compounds Contributing to Non-Cancer Toxicity.

NON-CANCER TOXICITY
Carbon disulfide
Toluene
Formaldehyde

Table IV. Key Compounds Contributing to Cancer.

CANCER
1,3-Butadiene
2-Nitropropane
Chloroform
Methylene chloride ($MeCl_2$)

AEERL/OCB will target sources which emit large quantities of "high-priority" VOCs and HAPs. These industry sources are summarized in Table V. Of the categories in Table V, AEERL/OCB, has selected surface coating technogies as one of its initial focus areas.

C. Types of Research and Evaluation Efforts in Targeted Areas

The types of research and evaluation work that the OCB undertakes in the targeted industry areas will be tailored to the specific compounds and processes used by these industries.

Table V. Key Industrial Sources

TARGET INDUSTRY AREAS	INDUSTRY
Plastics	Cellulosic manmade fibers
	Plastics materials and resins
	Plastic foam products
Synthetic rubber	Synthetic rubber
Petroleum refining	Petroleum refining
Industrial organic chemicals	Industrial organic chemicals
Surface coating	Motor vehicles and car bodies
	Wood household furniture
	Paper: coated and laminated
	Commercial printing, gravure
Reconstituted wood products	Reconstituted wood products
Pulp and paper mills	Pulp and paper mills
Mineral wool	Mineral wool

To the extent possible, knowledge and expertise gained in the earlier target areas will be applied to solve similar problems in the new target areas. Alternative, lower environmental impact compounds will be evaluated to replace conventional compounds (*e.g.*, n-methyl-2-pyrrolidone [NMP] as a potential replacement for $MeCl_2$ for paint stripping). Processes will be scrutinized and evaluated to identify modifications which may lead to more economical operations while reducing environmental impacts (*e.g.*, conversion of $MeCl_2$ vats for stripping paint from metal parts to a silica-based, gas-heated fluidized bed). The OCB's work will include the evaluation of P^2 approaches developed by others, the assessment of existing P^2 approaches to determine their applicability in new areas, the research, development, and demonstration of innovative P^2 approaches, and transfer of information about successful approaches to other potential users.

The vision of AEERL's Organics Prevention Research Program is to be the world leader in providing the techniques, technologies, cost-effective tools, and technical assistance needed to advance the use of P^2 approaches to reduce the emissions of high priority VOCs and HAPs to the atmosphere. The mechanisms (types of research) used by the OCB to reduce organic emissions are presented in Figure 1.

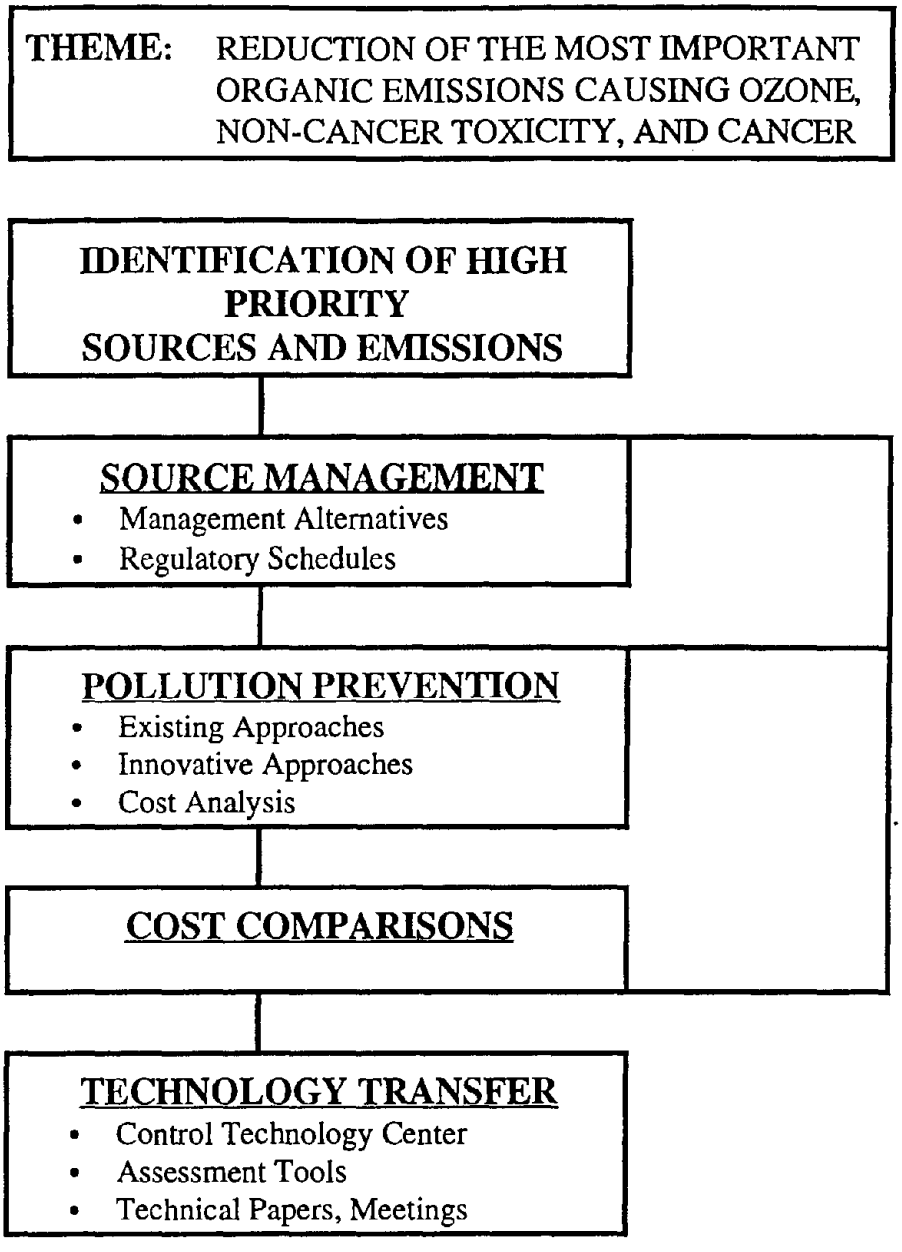

Figure 1. The organics prevention engineering research program

D. Coordination of Research and Evaluation Efforts

The magnitude and importance of the organic emissions problem, coupled with the OCB's limited fiscal resources and manpower, make coordination and cooperation with others doing related work absolutely essential. The OCB seeks to be aware of related research and evaluation efforts and to take these efforts into account in research planning. This is done by communicating personally with other researchers, participating in technical meetings, coordinating with trade associations, sponsoring information exchange forums (*e.g.*, this conference), sponsoring contractor efforts to locate and assess related research being conducted

elsewhere, and conducting searches of the technical literature related to targeted compounds, industries, and processes.

E. Technology Transfer

The OCB will continue to place emphasis on the expansion and enhancement of its technology transfer capabilities. Information developed by the research program is shared in a variety of ways with clients of the program, including EPA program offices, industries, and small businesses. To do so, the OCB will:

(1) Issue newsletters, conduct workshops and symposia, and support seminars in Research Triangle Park by outside experts; and

(2) Participate in the National Pollution Prevention Roundtable, trade association meetings, and other organizations whose objectives are the advancement of P^2 research and P^2 technology use by industry.

III. EXISTING SURFACE COATING PROJECTS

A. Introduction

This section briefly describes each of the OCB's surface coating projects that has been undertaken since 1990. Descriptions are organized first by industrial application, and then, for those that are more general in nature, by coating technology. Projects that are focused on technology transfer are presented in a separate section.

Generally, projects in each of the technical areas can be divided into four categories or types:

(1) Scoping Studies which characterize an industry or process and its emissions and identify P^2 opportunities to reduce those emissions. Scoping projects are ongoing for furniture restoration and repair, paper and other webs coating, printing, roofing, and consumer/commercial adhesives.

(2) Technology Assessment and Development Projects which evaluate the technical and economic feasibility of specific coating technologies or P^2 techniques. R&D projects are included in this category. Technology assessment and development projects are ongoing to evaluate very-low-VOC coatings for wood furniture manufacturing and auto body refinishing, to identify technical barriers to the use of radiation-cured and waterborne coatings, and to assess innovative ink-feed systems for printing, improved degreasing systems, cleanliness criteria for parts cleaning, and methods for determining the VOC content of consumer products.

(3) Demonstration Projects which investigate methods of reducing emissions in cooperation

with industrial partners. Demonstration projects are planned for coated and laminated substrate manufacturing, for the design of recirculating spray booths incorporating VOC concentration gradient phenomena, and for precision and non-precision cleaning.

(4) Technology transfer is an important type of project activity in OCB. Through technology transfer, the results of OCB's research are provided to the people who can use them, hopefully in a format that they can easily use. Technology transfer also provides OCB an opportunity to interact with its potential clients (*e.g.*, through workshops and conferences) to better understand their needs and the status of technology in many industries.

B. Industries

1. Wood Furniture
   a. Status and Future Developments in Very-Low-VOC Coatings for Wood Furniture Finishing. The objective of this project is to determine the status of R&D and market development for very-low-VOC coatings used for wood furniture finishing. Information has been gathered through contacts with resin suppliers, paint manufacturers, wood furniture manufacturers, and their trade associations. The technical barriers and concerns of industry about these coatings have been identified and explored[5]. [Bob McCrillis: (919) 541-2733]

   b. Accelerated Development and Market Penetration for Very-Low-VOC/HAP Wood Furniture Coatings. This project will be initiated during 1994. It will build on the results described in Section B.1.a. by selecting up to 10 promising coatings for further evaluation, developing a program to bring each of these to full marketability status, and testing these coatings in commercial facilities. This work is in progress. [Bob McCrillis: (919) 541-2733]

   c. Field Evaluation of an Innovative Coating Utilizing Reactive Diluents. This project's objective is to reduce volatile organic emissions from coating operations by demonstrating the technical and economic feasibility of using reactive diluents in alkyd and epoxy coating formulations. Organic emissions from coatings which are formulated with reactive diluents are less than those from traditional, solvent-based coatings since the reactive diluents react to form part of the coating and are not flashed off as carrier solvents. The reactive diluent, vernonia oil, has been successfully tested at the bench-scale at the Coatings Research Institute at Eastern Michigan University. Since vernonia oil is extracted from a rare African plant which is not readily cultivated, alternative reactive diluents derived from readily available soy and linseed oils to mimic the chemical and physical properties of vernonia oil have been developed. OCB will work with private paint researchers and coating retailers and users to field- or pilot-test innovative coatings using these diluents. This project is being performed cooperatively with South Coast Air Quality Management District (SCAQMD). The final report is available[6]. [Bob McCrillis: (919) 541-2733]

d. Furniture Refinishing and Repair. Information on non-process solvent use was evaluated for 15 industrial and commercial source categories to characterize VOC emissions and identify P^2 opportunities. Non-process solvents are used by industry, commercial operations, and/or individual consumers; they are not incorporated into a product or chemically modified as part of the manufacturing process. Project results will support a Report to Congress, required by §183(e) of the Clean Air Act Amendments of 1990 (CAAA), which addresses emissions of VOCs from consumer or commercial products. The report summarizing the 15 categories is available[7].

As a result of the 15-category evaluation, 5 source categories were selected for further study. One of these categories is Furniture Repair and Refinishing. For each category, a more detailed evaluation of emissions, emission sources, and P^2 opportunities is being completed. A final report detailing emissions and P^2 opportunities for this category is being prepared. (Mike Kosusko: (919) 541-2734]

e. Alternative Paint Strippers. Chemical paint stripping is a major source of air toxic and VOC emissions. $MeCl_2$, a halogenated solvent and air toxic compound which is not regulated as a VOC, is a predominant primary component in chemical strippers used by the furniture repair and refinishing industry. Researchers have been developing low-VOC coatings through continuing research, formulation adjustments, and application testing. The feasibility of using alterative strippers on these low-VOC coatings has not been documented. This research was conducted to evaluate the feasibility of using alterative chemical strippers to remove both existing and emerging low-VOC wood coatings. Performance and emissions associated with each alternative stripper were determined. The final report is available[8].
[Bob McCrillis: (919) 541-2733]

f. Waterborne Two-Component Epoxy Topcoats for Wood Furniture Finishing. A two-component water-based epoxy resin coating system containing less than 0.08 lb/gal (10 g/l) VOC has been developed as both clear and white-pigmented topcoats[9]. The VOC level, 0.08 lb/gal, is the minimum detection limit of the test procedure for VOC content. These topcoats have met most performance criteria including: (1) a VOC content of less than 0.08 lb/gal; (2) high gloss; (3) dry to touch in 10 minutes or less, dry to handle in 15 minutes or less; and (4) a 2H pencil hardness. A paper describing this research was presented at the First Low- and No-VOC Coatings Conference[10]. This project is cooperatively funded with SCAQMD. Research to develop a complete coating system (*i.e.*, sealer, stain, and topcoat) which utilizes these resins has been completed[11]. [Bob McCrillis: (919) 541-2733]

g. Evaluate P^2 Opportunities for Plywood and Particleboard MACT [Maximum Achievable Control Technology]. This Source Reduction Review Project (SRRP) targets the plywood and particleboard manufacturing industries which were included in the EPA's initial list of source categories of air toxic chemicals under Section 112

of the CAAA[d]. The industry was listed as a potential major source of manganese compounds and polycyclic organic matter. Emissions of HAPs from this industry have been associated with, but not limited to, the drying of binders. The objective of this project is to collect information regarding available and emerging options for P^2 in the plywood and particleboard industries. The final report is available[12]. [Betsy Howard: (919) 541-7915]

h. Quantification of VOC/HAP Emissions from Conversion Varnish Coatings and Demonstration of Formaldehyde-Free Alternative Coatings for Kitchen Cabinets. Wood and wood-veneered kitchen cabinets present a unique finishing challenge because they must be resistant not only to water, but also to many different detergents and foods, which may be spilled onto them during their lifetime. This has resulted in the wide use of conversion varnishes, which are acid-catalyzed reactive coating systems, that form strong, water resistant, attractive coatings by chemical reaction after they are applied. However, because these coatings are reactive, they release reaction byproducts during application and curing, as well as during their use in the indoor environment. This contributes to chemical emissions from the manufacturing facilities as well as emissions into the household indoor air.

Although several chemicals may be emitted from these coatings, the chemical of primary interest is formaldehyde, because it is a HAP, a VOC, a probable carcinogen, and an irritant. In addition, because the formaldehyde may be formed by the reaction that occurs after the coating is applied, its emission cannot be estimated from formulation information.

The objectives of this SRRP project are to: (1) Develop methods to measure cure emissions from conversion varnishes; (2) Measure cure emissions from several commonly used conversion varnishes to gain an understanding of their amount and composition; (3) Investigate alternative, lower-emitting coatings which can provide the water and chemical resistance and appearance necessary for this application. This includes coatings currently in use commercially, as well as promising emerging coatings; and (4) Demonstrate the most promising alternative, and measure emissions both in the manufacturing plant and in the household indoor environment, to evaluate their emissions compared to those of the conversion varnishes[c]. A conference paper summarizing results is available[13]. [Betsy Howard: (919) 541-7915; Bob McCrillis: (919) 541-2733]

2. Metal and Plastic Parts and Products Painting for Automotive and Other Applications
   a. Small Business Research Focus Group -- Metal Parts and Products Coating. In September 1994, the EPA and Research Triangle Institute (RTI) convened a 1-day focus group meeting to identify specific research needed to facilitate the adoption of

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[d] The SRRP is described in detail in Section A.9.b. of this paper.

P^2 technologies by small businesses that paint metal parts and products. The minutes of this focus group are being prepared. [Mike Kosusko: (919) 541-2734]

b. Applied Innovative Coatings Research. The purpose of this research is to identify a limited number of lower-emitting innovative coatings for metal and plastic automotive parts applications. These coatings may be either supplied by paint manufacturers or developed by university researchers, and will be demonstrated at the Department of Defense's (DoD's) National Defense Center for Environmental Excellence (NDCEE) in Johnstown, Pennsylvania. To supplement the research conducted at NDCEE, a technology diffusion plan has been developed for disseminating information developed during the testing program.

   A workgroup of over 40 industry and academic coating technology experts, the Coatings Research Forum, has been established to identify P^2 opportunities, and metal and plastic part coating formulations for testing. The minutes of the first Forum, August 1995, and the second Forum, August 1996, are being prepared.

   The first Coatings Forum identified four research opportunities: (1) Substitute Materials or Processes for High-VOC Adhesion Promoters for Coating of Thermoplastic Olefins; (2) Low- or No-VOC Coatings for Auto Body Refinishing; (3) Improved Line and Equipment Cleaning for Color Changes; and (4) Enhanced Coating Transfer Efficiency through Formulation Additives. Testing for the research area, Transfer Efficiency Additives, was completed June 1996.
   [Mike Kosusko: (919) 541-2734]

c. Demonstration of Solvent-Free Precision and Non-Precision Surface Cleaning Techniques. The purpose of this project is to identify candidate industrial processes in which conventional cleaning solvents can be replaced by non-organic solvents or by solventless technology, to demonstrate the alternative techniques, and then to compare them to conventional cleaning. Two reports detailing these demonstrations are available[14,15]. [Chuck Darvin: (919) 541-7633]

3. Auto Body Refinishing
   a. Reduction of Solvent Emissions from Auto Body Refinishing. The objective of this 1994 project is to demonstrate P^2 technology to reduce volatile organic emissions from auto body refinishing operations. Promising technologies such as high-volume low pressure spray guns, low VOC paints and primers, waterborne primers, and short wavelength infrared curing are available for this area. The demonstration will focus on technologies which can prevent emissions from small, dispersed, stationary area sources. The results of these tests will be made available to small companies that previously have not had access to control or prevention technologies. Work is underway and will be completed during mid-1996. [Geddes Ramsey: (919) 541-7963]

4. Architectural and Industrial Maintenance (AIM) Coatings
   a. Innovative Architectural and Industrial Maintenance (AIM) Coatings Assessment. The goal of this 1994 project is to identify and target AIM coating applications with high environmental risks, identify potential research partners involved with these applications, solicit their participation, and evaluate innovative, low-emitting coatings at their facilities. A report detailing results of this evaluation is being prepared. [Mike Kosusko: (919) 541-2734]

5. Reinforced Plastics (Gel Coats)
   a. Evaluation of Pollution Prevention Techniques to Reduce Styrene Emissions from Open Contact Molding Processes. At 21,000 tons (19,050 tonnes) annually, styrene is the 13th ranked organic compound in the Toxic Release Inventory (TRI) on a mass emission basis; it is also carcinogenic. Styrene is known to be a significant HAP emitted from the reinforced plastic composites manufacturing source category. Limited test data are available to quantify styrene emissions from reinforced plastic composites fabrication. This is due to the nature of fabrication processes and facilities, which produce significant fugitive styrene emissions. The goal of this SRRP is to identify and evaluate testing procedures to quantify styrene emissions from fabrication processes[d]. These testing procedures will be used to quantify the emissions reduction possible from source reduction techniques. The final report is available[16]. [Carlos Nuñez: (919) 541-1156]

   b. Evaluation of P^2 Techniques to Reduce Emissions from Open Contact Molding Processes. The purpose of this SRRP is to evaluate P^2 techniques to reduce stryene emissions from open contact molding processes[d]. This process is one of the most common production processes used by the fiber-reinforced plastics and composites (FRP/C) industry. It is used to manufacture boats, bathtubs, shower stalls, truck body parts, swimming pools, storage tanks, etc. The open contact molding process is one of the FRP/C processes that consumes the most polyester resins. It also has the greatest potential for emitting styrene due to the spraying equipment used and the openness of the process. The objective of this test is to use emission measurements and mass balance calculations to quantify and validate the effects of several P^2 techniques, specifically gel coat/resin formulations and application equipment, on styrene emissions from the open contact molding process. The project final report is anticipated for 1997. [Geddes Ramsey: (919) 541-7963]

6. Adhesives
   a. Enhancing the Market Penetration of Waterborne and Other Low-Solvent Consumer/Commercial Adhesives. This project has been funded to identify, develop, and demonstrate new, innovative waterborne and low-solvent adhesive systems using recently discovered and other innovative raw materials. Promising adhesive systems and potential industrial and academic partners will be identified. A research center may be established at a university or non-profit research institute to develop and/or evaluate innovative adhesive formulations. [Chet Vogel: (919) 541-2827]

b. Retrofit of Existing Solvent-based Flexible Substrate Coating Equipment to Use Water-based Coating Systems. The coated and laminated substrate manufacturing industry makes a wide variety of pressure sensitive products such as paper (masking), cloth (duct), and cellophane tapes, tags, and labels, and a number of exotic laminated products. It was selected for study because of significant air emissions of methyl ethyl ketone (MEK) and toluene reported in the 1990 Toxics Release Inventory, *i.e.*, it is the #1 source for MEK (8,050 tons/yr [7,300 Mg/yr]) and the #3 source for toluene (13,000 tons/yr [11,800 Mg/yr]). A focus group, including members of the Pressure Sensitive Tape Council (PSTC), the Tag and Label Manufacturers Institute, and academic and state environmental experts, helped OCB identify opportunities for significant reductions of volatile HAP emissions in this industry.

The use of solventborne coatings (*e.g.*, adhesives) was identified as the primary source of the industry's toluene and MEK emissions. The objective of this project is to evaluate the quality and economic viability of waterborne adhesives when used to replace solventborne adhesives on flexible substrates by modifying existing coating equipment. A report documenting background issues for this project is available[17]. The high level of industry participation through the PSTC allowed case studies to be completed and published[18,19,20]. [Chet Vogel: (919) 541-2827]

c. Small Business Research Focus Groups -- Lower-Emitting Adhesives for Automotive Interior Trim Applications. In August 1995, the EPA and RTI convened a 1-day focus group meeting to identify P^2 research needs associated with adhesives used in the the automotive interior manufacturing industry. [Chet Vogel: (919) 541-2827]

d. Textile Screen Printing -- Alternative Platen Adhesives. As a result of the 15 category evaluation, 5 categories were selected for further study (see Section B.1.d.). For each of the five categories (Textile Manufacturing in this case), a more detailed evaluation of emissions, emission sources, and P^2 opportunities was completed. A report detailing emissions and P^2 opportunities for the textile industry is being prepared.

Two evaluations were completed as a result of the textiles report. The feasibility of substituting waterborne platen adhesives for solvent-based adhesives in aerosol cans was evaluated, first for automatic and then for manual spraying systems. A paper is available describing the demonstration of automatic spraying systems.[21] Reports detailing the successful reduction of emissions through the use of waterborne platen adhesives are being prepared. [Mike Kosusko: (919) 541-2734]

e. Coated and Laminated Paper Equipment Cleaning. The rationale for this project is similar to that for the "retrofit" project described earlier under in Section B.6.b. However, the focus of this project is on the second largest source of MEK and toluene emissions in the industry, equipment cleaning. The objectives of this project are to identify and evaluate improved methods for cleaning process equipment surfaces,

recommend candidate demonstration projects, conduct demonstrations, and transfer technical findings to the small businesses in the industry. A report detailing emissions characterization and P^2 opportunities is available[22]. A report on demonstrated alternatives is also available[23]. [Mike Kosusko: (919) 541-2734]

7. Printing and Publishing
   a. Characterization and Modification of Microstructure in Waterborne Inks Stabilized by Polymeric Surfactants. The objective of this project is to develop the use of polymeric surfactants to stabilize the microstructure in, and influence the physical properties of, waterborne inks. The focus will be the enhancement of the performance of traditional inks, not the reformulation of inks. Specific research will include: 1) characterization of the microstructure of waterborne ink systems; 2) correlation of the microstructure with physical properties (*e.g.*, stability, viscosity, ink/substrate compatibility); 3) identification of the dominant structure-property relationships; and 4) modification of the microstructure by adjusting the molecular characteristics of polymeric surfactants to produce a system with the desired properties (*e.g.*, gloss, heat resistance, and opacity). VOC and air toxic emission reductions will result from this project if it is successful. [Kaye Whitfield: (919) 541-2509]

   b. Innovative Ink Feed Systems. This project is part of the SRRP (see Section B.9.b. below). It is focused on the flexography and gravure segments of the printing and publishing industry. Many flexographic and gravure facilities are major sources of HAPs, especially when compared to offset lithography, letterpress, or screen printing facilities. The systems (*e.g.*, piping, tanks, and mixers) used to feed ink to printing presses and their subsequent cleaning requirements are the source of substantial volatile HAP emissions. Alternative feed systems could substantially reduce these emissions. A project report is available[24]. [Carlos Nuñez: (919) 541-1156]

8. General
   a. Assessment of Pollution Prevention Opportunities in Five Industries. In this small, cooperative project with the SCAQMD in Los Angeles, California, emissions and P^2 opportunities have been assessed for the following five industries, all of which use surface coatings:

      1) Architectural and Industrial Maintenance Coatings;
      2) Consumer/Commercial Adhesives;
      3) Rotogravure Printing;
      4) Flexographic Printing; and
      5) Graphic Arts.

   The final report for this project is available[25]. [Mike Kosusko: (919) 541-2734]

b. Source Reduction Review Program (SRRP) Focus Groups. The purpose of this SRRP project is to identify P^2 opportunities via focus group input for 3 of the 17 SRRP categories. Of the three, two are surface coating categories (*i.e.*, Paper and Other Webs, and Reinforced Plastics). The other category is Integrated Iron and Steel Manufacturing. Focus groups have included the participation of industrial, governmental, and academic experts to achieve a broad perspective. [Carlos Nuñez: (919) 541-1156]

c. Evaluation of Alternative Paint Stripping Technologies Used In Aircraft and Space Vehicles. Low toxicity and low-VOC paint stripper alternatives for metal reworking were identified, evaluated, and compiled in this 1994 SRRP project under an Interagency Agreement with the National Aeronautics and Space Administration (NASA)[d].This project focused on the evaluation and testing of depainting systems which do not use $MeCl_2$ or any of its sister polluting agents. [Geddes Ramsey: (919) 541-7963]

d. Support to NSF University Cooperative Research Center in Surface Coatings. This project would provide support to the Industry/University Cooperative Research Center in Coatings (I/UCRCC) established at Eastern Michigan University in 1990 by the National Science Foundation (NSF). The Michigan Molecular Institute (MMI) became affiliated with the Center in 1991 and North Dakota State University (NDSU) became affiliated in 1994. Nine companies and organizations are currently members of the Center; growth by five to eight new members is planned. The Center's current scientific and technological program objectives are grouped within principal areas of expertise:
   - To demonstrate new concepts in polymer synthesis and crosslinking
   - To learn principles of the physical phenomena that are critical to coatings technology
   - To improve characterization methods for coatings

   [Bob McCrillis: (919)541-2733]

C. Technologies

1. Radiation-curable Coatings
   a. Technical Barriers to the Use of Radiation-cured and Waterborne Coatings. This project is part of the SRRP and has focused on wide-web flexography and metal can manufacturing[d]. The use of radiation-cured (*e.g.*, ultraviolet [UV]-cured and electron beam-cured) or waterborne coatings is a P^2 option for several SRRP source categories. However, technical barriers to their broadened usage exist, including concerns about toxicity and the difficulty of coating complex parts using radiation-cured coatings. The objective of this project is to identify and characterize these technical barriers and to identify critical research to overcome them. Results of this project will be available both as a project report and a journal article[26]. [Carlos Nuñez: (919) 541-1156]

b. Focus Group Meeting for Metal Can Manufacturers and Flexographic Printing. EPA has focused significant effort on investigating and evaluating alternative coating formulations for several industries, specifically focusing on radiation-curable coatings. This work is in support of the SRRP, which is designed to ensure that source reduction and multimedia issues are considered during the development of upcoming air, water, and hazardous waste standards. Two of the 17 SRRP industrial categories were the focus of this meeting. A report on the research opportunities for both industries will be published. [Carlos Nunez: (919) 541-1156]

c. Basic R&D on Radiation-cured Coatings. The results of the 'Barriers' project (Section C.1.a.) are being used to target research opportunities for radiation-curable coatings. [Carlos Nuñez: (919) 541-1156]

2. Powder Coatings
   a. Application of DoD Powder Coating Expertise to Civilian Applications. The objective of this 1994 Environmental Technology Initiative (ETI) project is to improve the competitiveness of small businesses by allowing them to coat their products more efficiently by using powder coatings whenever they are technically and economically feasible. Paint powder is electrostatically applied to the substrate. Overspray is collected and reused. The powder coated parts are then heat-cured in an oven or with infrared lamps. The process eliminates VOC and many HAP emissions and avoids generation of paint booth wastewater. The powder coating expertise developed by DoD has been applied to civilian applications. The project report will become available during 1997. [Kaye Whitfield: (919) 541-2509]

3. Paint Spray Gun Enhancements
   a. Evaluation of Ultra-Low-Volume (ULV) Spray Gun System. The objective of this project was to evaluate an ULV spray gun system. Tests have been completed cooperatively with the U.S. Air Force at Warner-Robins Air Force Base, Georgia. Qualitative results of the test are promising. An improvement of paint utilization efficiency was attributed to the enhanced paint lay down provided by the gun. This and the ability to spray high viscosity paints (which contain fewer solvents) have led to a 50% reduction in VOC emissions. The project report is available[27]. [Chuck Darvin: (919) 541-7633]

   b. Spray Gun Cleaning. The purpose of this project is to compare emissions from two types of paint spray gun cleaning equipment (*i.e.*, open- and closed-systems) to each other and to those of current cleaning practices. This project has been in support of EPA's Control Technology Center (CTC). The CTC provides technical support to local, state, and EPA Regional environmental personnel, small businesses, and international clients. It is co-sponsored by AEERL and EPA's Office of Air Quality Planning and Standards (OAQPS). The final report will be available in 1997. [Geddes Ramsey: (919) 541-7963]

4. Partitioned, Recirculating Spray Booth. This project is presented even though it is not P^2 since it complements OCB's P^2 projects in surface coating. Recirculation in paint spray

booths has been recognized for many years as a means of reducing the volume of spray booth exhaust. This allows the use of a smaller control device, hence reducing air pollution control costs (*i.e.*, equipment and energy costs). Partitioning of the spray booth exhaust stream takes advantage of the VOC concentration gradient that exists vertically across the booth exit. VOCs stratify in the booth and their concentration is greatest closer to the floor. By pulling the booth exhaust stream from the bottom portion of the booth and the recirculating stream from the top portion of the booth, the concentration of the exhaust stream can be enhanced, perhaps removing the same mass of pollutants in a smaller exhaust volume than is possible in a traditional recirculating booth. Preliminary field tests have shown the feasibility of reducing controlled air volumes by 50 to 75% below non-recirculating booths.

A demonstration of the stratified recirculation concept at the U.S. Marine Corps Maintenance Depot near Barstow, California, is complete. During the demonstration, an existing spray booth was modified to use both recirculation and partitioning. A movable plenum was used to evaluate the optimum height for flow partitioning. An end-of-pipe control technology was evaluated in conjunction with the spray booth demonstration. Spray booth exhaust feeds to a control device which uses UV light to destroy organic compounds absorbed on a catalytic substrate, scrubbing with ozonated water, and a final activated carbon polishing step. [Chuck Darvin: (919) 541-7633]

D. Technology Transfer

1. The Surface-Coating-Free Materials Workshop. This workshop was held July 1991 to explore the potential for development and use of materials that would not need to be coated during manufacture or recoated during use. If such materials were to come into widespread use, VOC and air toxic emissions associated with surface preparation (cleaning), coating, and paint stripping before recoating could be avoided. The proceedings of this workshop are available[28]. [Mike Kosusko: (919) 541-2734]

2. The 1st Pollution Prevention Conference on Low- and No-VOC Coating Technologies. This conference was held in San Diego, California, in May 1993 to provide a forum for exchanging technical information on innovative coating technology and to allow EPA to interact with industry, academia, and others interested in surface coating technology. Conference proceedings are available[29]. [Mike Kosusko: (919) 541-2734]

3. The 2nd Pollution Prevention Conference on Low- and No-VOC Coating Technologies. This paper has been prepared for the Proceedings of the 2nd Biennial International Low- and No-VOC Coating Technologies Conference held March 1995 in Durham, North Carolina. Proceedings of the Conference will be available. A third conference is tentatively planned. [Mike Kosusko: (919) 541-2734]

4. Coatings Alternatives Guide (CAGE). In response to environmental regulations, coating users have been acting to reduce their emissions of HAPs and VOCs from painting operations. Although coating suppliers are rapidly developing new, low- and no-VOC coatings, end-users, particularly small business, are frequently unaware of new products and

assistance with sorting through hundreds, if not thousands, of available low-emitting products to determine which products can be of benefit in specific applications.To address this need, RTI and EPA have cooperatively developed a tool, The Coating Alternatives Guide (CAGE), for small businesses. CAGE is being developed to assist coating users in identifying and learning about lower-emitting, technically innovative, cost-effective coatings. It is designed to provide information on coating equipment and alternatives in a user-friendly, question-driven format. To date, CAGE has focused on metal substrates. Future modules will include nonmetallic substrates such as plastics and wood. CAGE is available on the INTERNET and in a DOS version designed for use on a personal computer. CAGE contains an expert system and background information. The CAGE program is designed to meet both customer demands and tough environmental regulations. CAGE has been described in several conference papers[30,31]. [Mike Kosusko: (919) 541-2734]

5. Adhesives Alternatives Guide (AAGE). The purpose of this project is to provide information on the formulation and use of low- and no-VOC substitutes for conventional, solvent-based adhesives. AEERL plans to develop a software package call AAGE (The Adhesives Alternatives Guide) to provide technical assistance to regulators and small businesses. This software will provide information on the formulation and use of low- and no-VOC substitutes for conventional solvent-based adhesives. Special emphasis will be placed on the environmental, health, and safety characteristics and impacts of potential substitutes. These characteristics and impacts will be compared to those of conventional solvent-based adhesives. Emission reduction potentials due to the use of alternate processes or products will also be estimated. Specifying an end product will show the conventional method of manufacture and several more environmentally friendly means of producing this product. AAGE has been described in a journal article[32]. [Chet Vogel: (919) 541-2827]

6. Solvent Alternatives Guide (SAGE). The objective of this program is to provide a simple method of identification for cleaning options of low-polluting industrial surface cleaning alternatives. This software program uses the speed and capability of the computer to evaluate a large number of operating parameters and conditions to identify the most viable surface cleaning option for a given situation. The program is available via SAGE Web Site at http://clean.rti.org/. [Chuck Darvin: (919) 541-7633]

IV. SUMMARY AND CONCLUSIONS

The Organics Control Branch (OCB) has a P^2 program which involves industries which have significant VOC and HAP emissions from surface coating and cleaning operations. These industries include wood furniture manufacturing, coated and laminated substrate manufacturing, and printing and publishing. Each of these industries has common concerns, and it is hoped that the results of our work with one industry will be useful to other industries. This paper summarizes surface coating research, development, and demonstration activities in OCB. The input of a broad spectrum of industry, academic, and other experts, such as the attendees at this symposium, is needed to continue to enhance the focus, quality, and content of OCB's current and future research activities.

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SESSION 2

REGULATORY UPDATE

PAPERS PRESENTED:

"Regulatory Climate"
(Paper not available for publication.)
by
Bruce Jordan
Director, U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Durham, North Carolina

"Low VOC Measurements, HAP Measurements in Paints, Questions, Questions, Questions"
by
K. Hiroshi Fujimoto
Advanced Technologies of Michigan
West Bloomfield, Michigan

"Developments in European VOC Emission Regulations"
by
Bob Ollerenshaw
Paint Research Association
Middlesex, United Kingdom

"Coating Alternatives Guide"
by
Jesse Baskir
Research Triangle Institute
Research Triangle Park, North Carolina

LOW VOC MEASUREMENTS,

HAP MEASUREMENTS IN PAINTS,

QUESTIONS, QUESTIONS, QUESTIONS!

BY

K. HIROSHI FUJIMOTO

ADVANCED TECHNOLOGIES OF MICHIGAN

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

I WISH TO THANK THE FOLLOWING INDIVIDUALS FOR THEIR HELP AND CONTRIBUTIONS:

DR. SWAMINATHAN RAMESH, BASF

DR. JOE BENGA, PPG

DR. KEITH OLSON, GENERAL MOTORS

MY BACKGROUND AND EXPERIENCES

⇒ TECHNICAL MANAGER, ANALYTICAL SERVICES, BASF CORPORATION, FOR 35 YEARS

⇒ INVOLVED IN VOC TEST MEASUREMENTS SINCE 1977 OR ABOUT 18 YEARS

⇒ CHAIRMAN, ASTM SUBCOMMITTEE D-1.21 ON ANALYSIS OF WHOLE PAINT

⇒ HELPED DEVELOP AND WRITE ASTM TEST METHODS USED IN US-EPA REFERENCE METHOD 24 FOR VOC MEASUREMENTS IN PAINTS

⇒ BI-ANNUALLY, RUN THE "ASTM PAINT VOC MEASUREMENT WORKSHOP" THROUGHOUT THE US FOR THE LAST 10 YEARS

⇒ RETIRED FOR 2 YEARS

⇒ PRESIDENT, K. HIRO FUJIMOTO, CONSULTANT, INC.

⇒ DIRECTOR, ADVANCED TECHNOLOGIES OF MICHIGAN WHICH SPECIALIZES IN VOC AND HAP MEASUREMENTS OF PAINTS AND NON-PAINT PRODUCTS.

OUTLINE

⇒ QUICK REVIEW OF THE VOC SITUATION.

⇒ ASTM TEST METHODS USED IN US-EPA's REFERENCE METHOD 24 FOR THE MEASUREMENT OF VOCs.

⇒ CALCULATION OF VOC.

⇒ SHOULD THE "MINUS WATER" CONCEPT BE DROPPED?

⇒ DIRECT METHOD TO DETERMINE VOCs.

⇒ MEASUREMENTS OF HAPs IN PAINTS.

⇒ RULE 311, A GC METHOD TO DETERMINE HAPs.

⇒ THE USE OF HS/GC/MS TO DETERMINE HAPs.

⇒ CONCLUSION

BACKGROUND

⇒ ASTM SUBCOMMITTEE D-1.21 HAS BEEN FORTUNATE IN BEING ABLE TO TAKE AN ACTIVE PART IN THE DEVELOPMENT OF TEST METHODS NEEDED TO MEASURE VOCs.

⇒ BACK IN 1977-1978, WE WERE TRYING TO FIND COMPROMISE TEST METHODS WHICH WOULD COVER 80% OR 90% OF THE PAINTS IN USE AT THE TIME.

⇒ THANKS TO US-EPA's JIM BERRY's FORESIGHT, AND GARY McALISTER'S INPUT, WE WERE ABLE TO WORK TOGETHER TO DEVELOP REFERENCE METHOD 24.

⇒ IT HAS BEEN AN EDUCATION AND A SYMBIOTIC RELATIONSHIP FOR ALL OF US.

REGULATIONS TO LOWER

VOCs AND HAPs

ARE EXCELLENT TOOLS TO CLEAN UP OUR POLLUTED AIR

HOWEVER,

WITHOUT ACCURATE, RELATIVELY EASY TO RUN, TEST METHODS, ENFORCING THE REGULATIONS BECOMES DIFFICULT AND/OR IMPOSSIBLE.

<u>THIS IS THE PROBLEM FACING US TODAY.</u>

IN 1978, WHEN WE WERE TRYING TO DEVELOP AN ACCEPTABLE TEST TO MEASURE VOCs:

⇒ **26% NONVOLATILE THERMOPLASTIC ACRYLICS WERE BEING USED.**

⇒ **THE VOCs WERE AROUND 5.0-6.0# / GAL.**

⇒ **THERE WERE VERY FEW WATER-REDUCIBLE PAINT SYSTEMS IN USE.**

TODAY, THERE HAS BEEN AN 80%-100% IMPROVEMENT OR A SIGNIFICANT DECREASE IN THE AMOUNT OF VOCs IN PAINTS THANKS TO THE GENTLE PRODDING OF JIM BERRY AND HIS STAFF:

⇒ **HIGH SOLIDS PAINT SYSTEMS IN BOTH THE WATER- AND SOLVENT- REDUCIBLE (60-70% NV) ARE BEING USED.**

⇒ **THE VOCs ARE IN THE NEIGHBORHOOD OF 3.0-2.8# / GAL OR LESS AND DROPPING**

⇒ **THERE IS PRESSURE TO GET LOWER VOCs UNDER:**

- **AVERAGING**
- **BUBBLING**
- **BANKING (VOC CREDITS)**
- **OFF SETTING**

⇒ **POWDER COATINGS WITH NO VOCs**

⇒ **MULTI-COMPONENT, LOW OR NO VOC, PAINT SYSTEMS**

IS RM 24 APPLICABLE TO TODAY'S PAINT TECHNOLOGIES?

⇒ TEST METHODS ARE OK, BUT CALCULATIONS DISTORT PRECISION SINCE THE SLIGHTEST VARIATIONS IN EACH OF THE TEST METHODS ARE COMPOUNDED AND EXAGGERATED.

⇒ THERE TENDS TO BE GREATER DISCREPANCIES IN THE DETERMINATION OF HIGH % WATER CONTENT.

⇒ LOW VOC NUMBERS, I.E. AN 1% VARIATION IN TEST RESULT FOR A PRODUCT WHICH CONTAINS 10% VOC IS A DIFFERENCE OF 10%.

⇒ AS THE VOCs GO LOWER AND % NONVOLATILES GO UP, WE ARE SUBTRACTING FROM LARGE NUMBERS TO OBTAIN SMALL NUMBERS WHICH EXACERBATES THE SLIGHTEST VARIATION IN TEST RESULTS.

⇒ FOR LOW VOC CONTAINING PAINTS, WIDE VARIATION IN REPEATABILITY AND REPRODUCI BILITY ARE SEEN.

⇒ COMMON TO SEE NEGATIVE VALUES OBTAINED FOR LOW VOC CONTAINING PAINTS.

What VOC is analytically...

A value or number obtained *under specified test conditions*.

RM 24 is a Compromise Between:

- Complexity of test methods
- Use of ASTM test methods which give results closest to the theoretical values (formula).
- Time required
- Equipment needed

US-EPA's REFERENCE METHOD 24 REFERS TO THE FOLLOWNG ASTM TEST METHODS TO DETERMINE PAINT VOCs:

⇒ ASTM D 1475 "DENSITY OF PAINT, VARNISH, LACQUER, AND RELATED PRODUCTS"

⇒ ASTM D 2369 "VOLATILE CONTENT OF COATINGS

⇒ ASTM D 3792 "WATER CONTENT OF WATER-REDUCIBLE PAINTS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH"

⇒ ASTM D 4017 "WATER IN PAINTS AND PAINT MATERIALS BY KARL FISCHER METHOD"

⇒ ASTM D 4457 "DETERMINATION OF DICHLOROMETHANE AND 1,1, 1-TRICHLOROETHANE IN PAINTS AND COATINGS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH"

- ⇒ ASTM D 5095 "NONVOLATILE CONTENT IN SILANES, SILOXANES AND SILANE-SILOXANE BLENDS USED IN MASORARY WATER REPELLENT TREATMENTS"

- ⇒ ASTM D 5403 "VOLATILE CONTENT OF RADIATION CURABLE MATERIALS"

- RECENTLY APPROVED

REMEMBER, EACH ONE OF THESE TEST METHODS HAVE A PRECISION STATEMENT

REPEATABILITY

THE MEASURE OF THE SAME CHEMIST'S ABILITY TO REPEAT RESULTS ON THE SAME DAY AND ON ANY FOLLOWING DAY.

REPRODUCIBILITY

HOW ONE CHEMIST IN ONE LABORATORY CAN REPRODUCE THE RESULTS OBTAINED BY ANOTHER CHEMIST IN ANOTHER LABORATORY.

IN SUMMARY

THESE ARE PLUS AND MINUS VALUES.

General Expression

$$\text{VOC} = \frac{\text{(weight percent of total volatiles less water less exempt solvents) x (density of coating)}}{\text{100\% - (volume percent of water) - (volume percent of exempt solvents)}}$$

General Expression

- $$VOC = \frac{(W_o) \times (D_c)}{100\% - V_w - V_{ex}}$$

$$= \frac{(W_v - W_w - W_{ex}) \times (D_c)}{100\% - (W_w) \times (D_c / D_w) - (W_{ex}) \times (D_c / D_{ex})}$$

VOCs ARE REPORTED AS:

SOLVENT-REDUCIBLE COATINGS

⇒ **GRAMS / L**

⇒ **POUNDS / GAL**

WATER-REDUCIBLE COATINGS

⇒ **GRAMS / L minus WATER**

⇒ **POUNDS / GAL minus WATER**

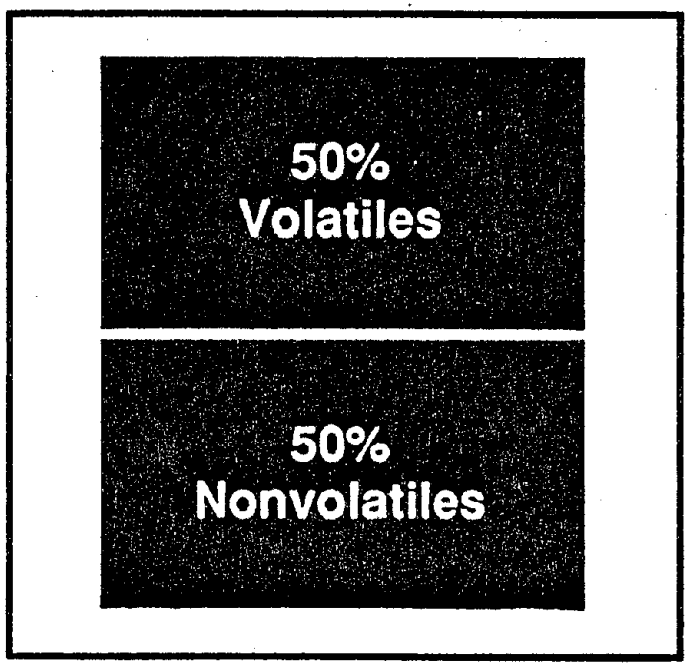
FUTURE GOAL--ALL PAINTS & COATINGS

⇒ **MASS OF VOC / MASS APPLIED COATING SOLIDS**

WHY THE "MINUS WATER" CONCEPT?

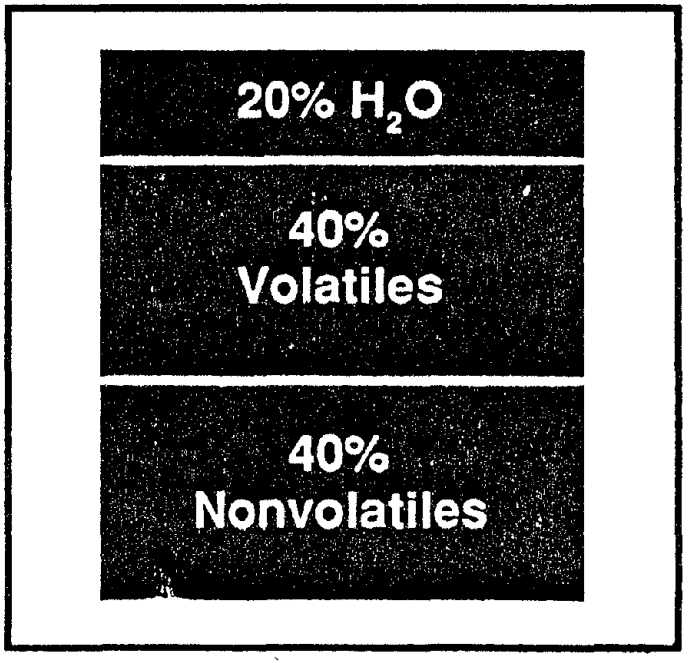
Minus Water Calculation

% Volatiles	**50.0%**
VOC (with water)	**4.3 lbs./gal.**
VOC (minus water)	**4.3 lbs./gal.**



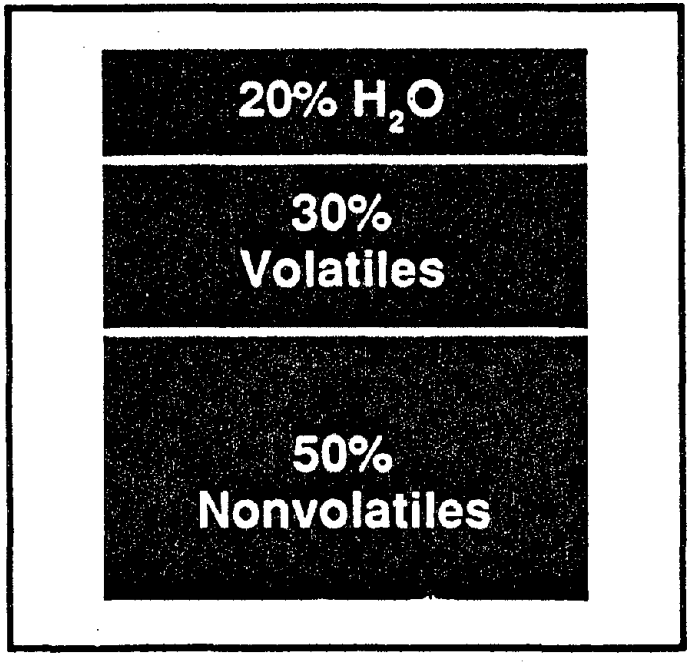
Minus Water Calculation

% Volatiles	**60.0%**
VOC (with water)	**3.4 lbs./gal.**
VOC (minus water)	**4.3 lbs./gal.**



Minus Water Calculation

% Volatiles	50.0%
VOC (with water)	2.6 lbs./gal.
VOC (minus water)	3.4 lbs./gal.



THEREFORE,

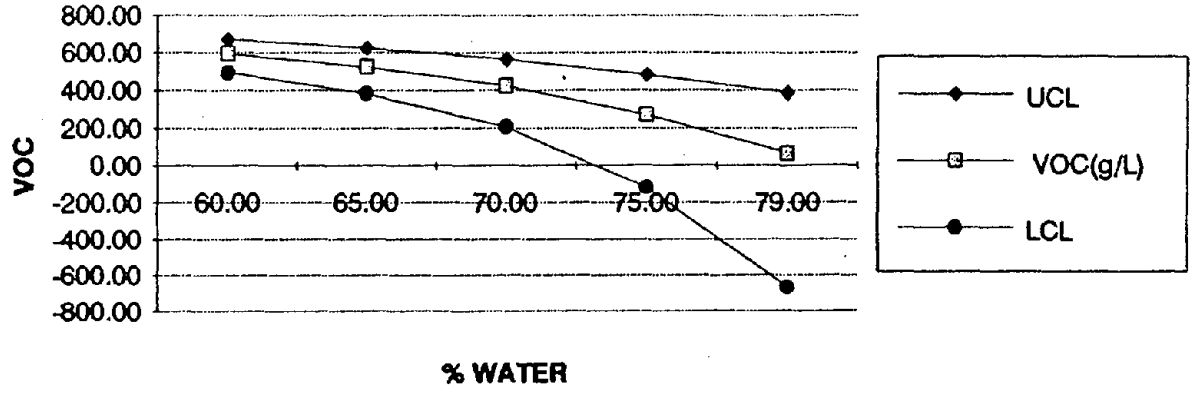
IT IS RECOMMENDED THAT:

⇒ **FOR LOW VOC PAINTS AND COATINGS, DROP THE "MINUS WATER" CONCEPT.**

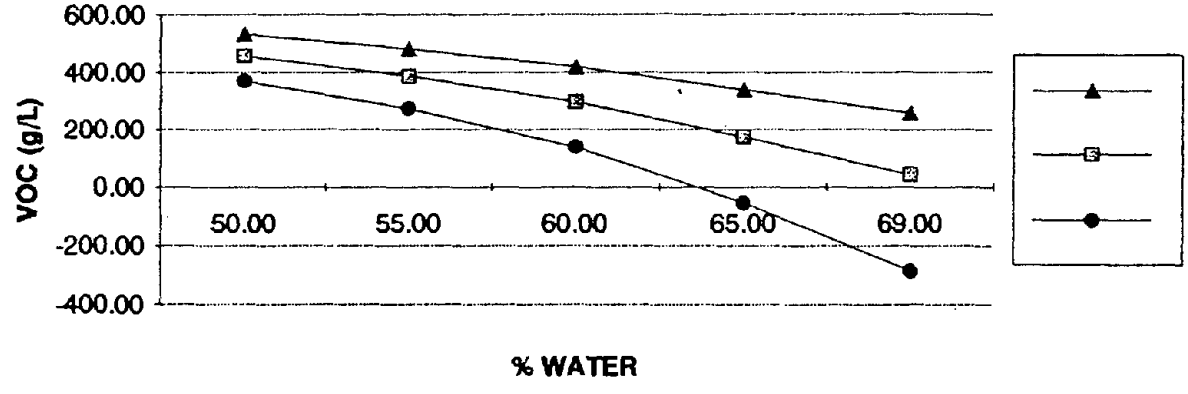
⇒ **THE WIDE VARIATION IN RESULTS ARE DUE TO THE CALCULATIONS.**

HERE ARE MY REASONS!!

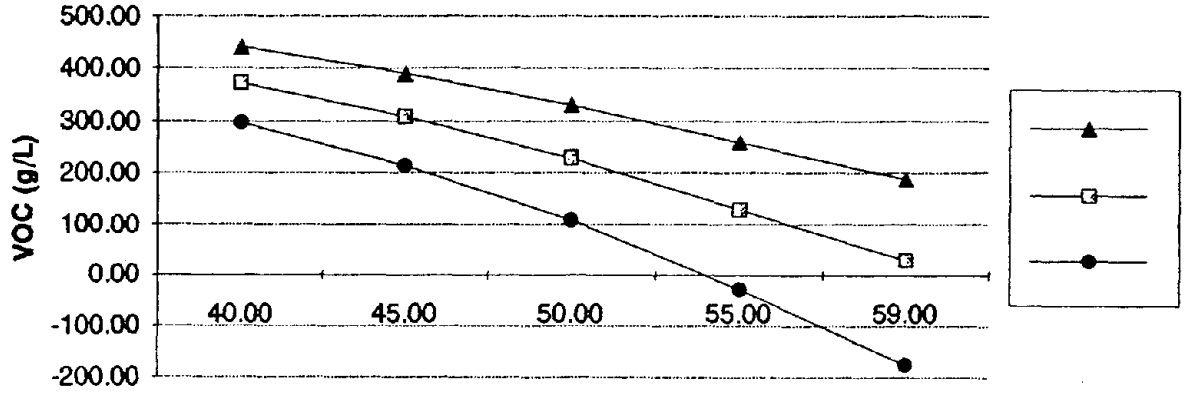
BETWEEN LABORATORY VOC RANGES @ 20 % NV

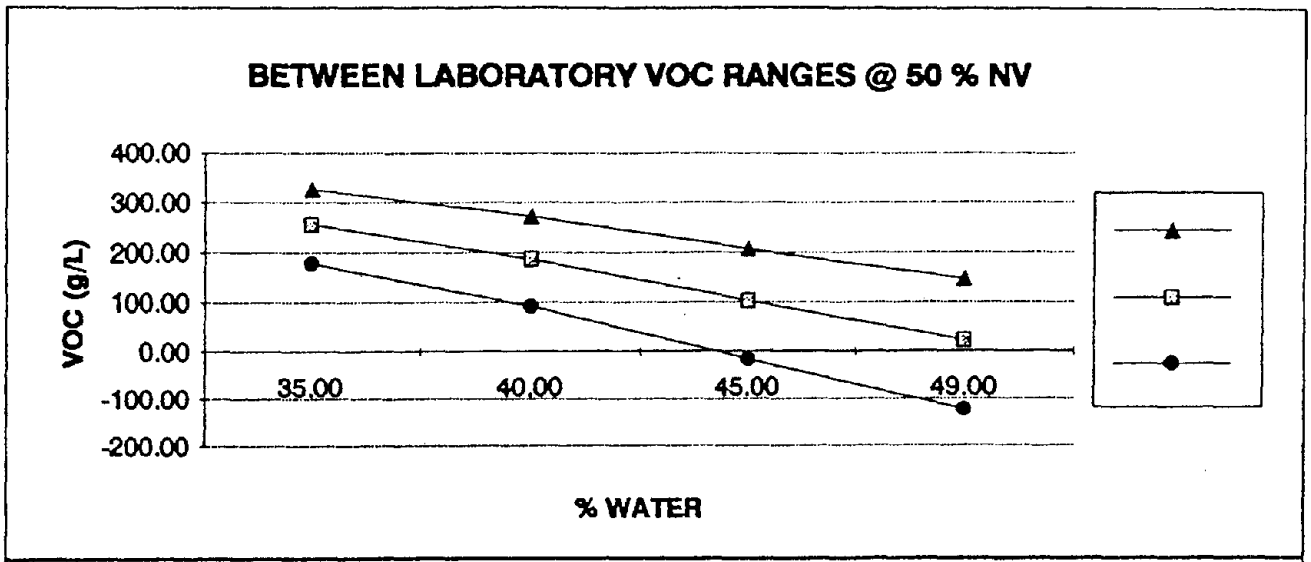


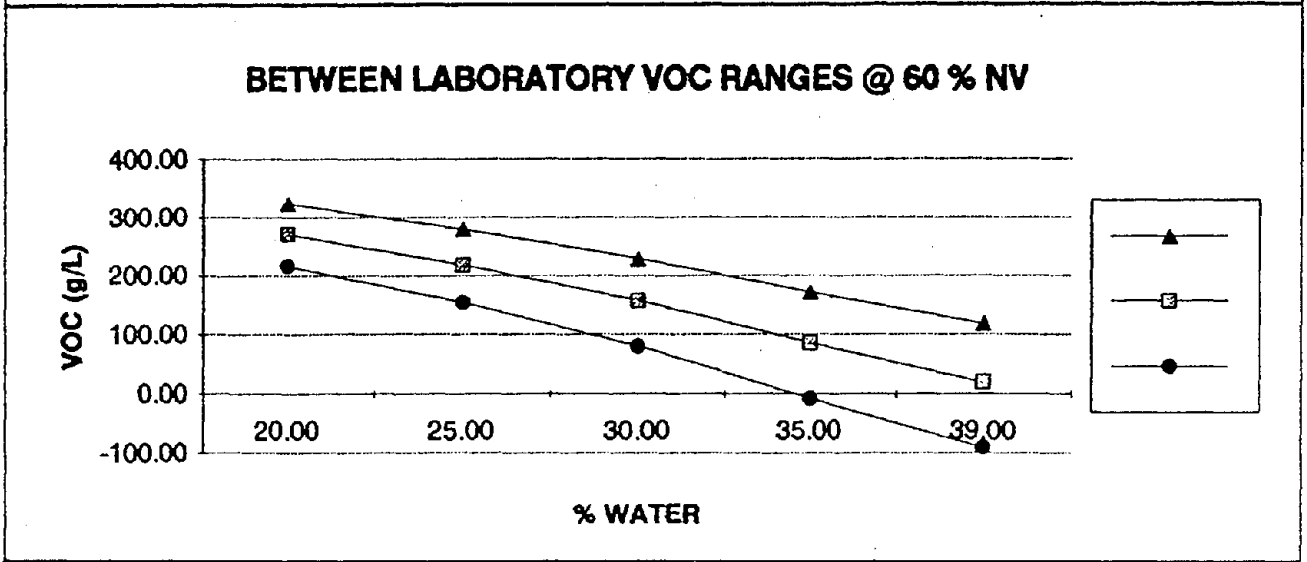
BETWEEN LABORATORY VOC RANGES @ 30 % NV

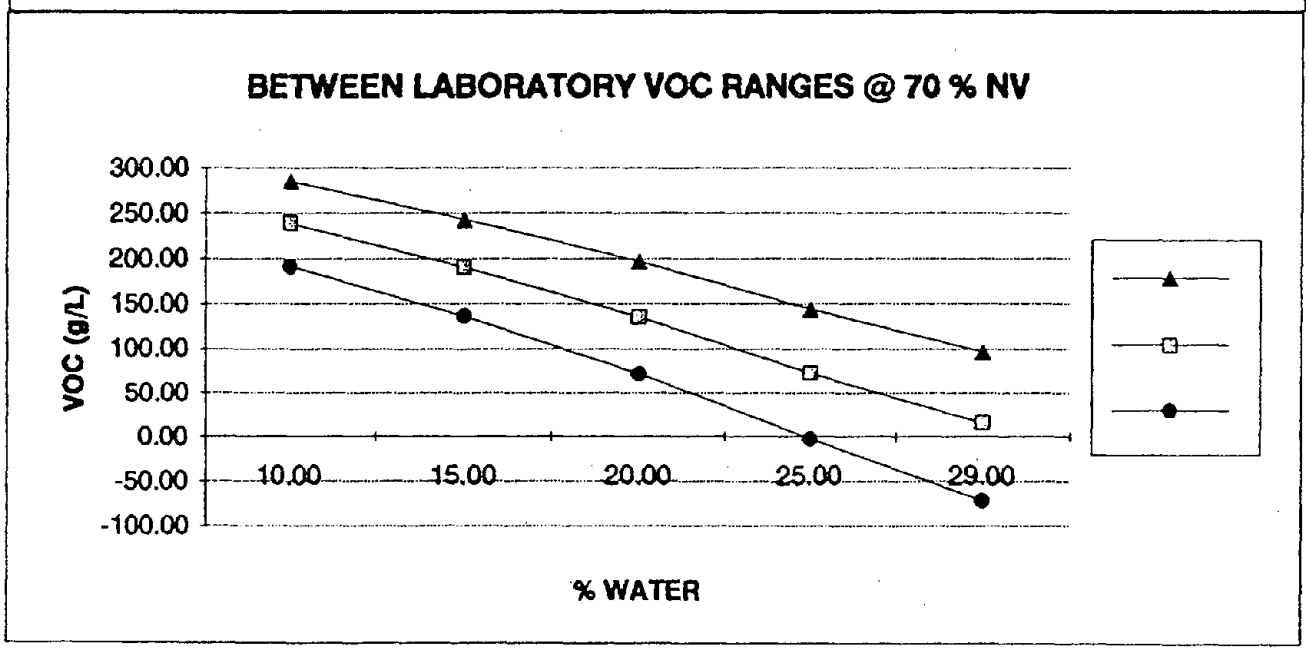


BETWEEN LABORATORY VOC RANGES @ 40 % NV




BETWEEN LABORATORY VOC RANGES @ 50 % NV
400.00
300.00
200.00
100.00
0.00
-100.00
-200.00
VOC (g/L)
35.00
40.00
45.00
49.00
% WATER


BETWEEN LABORATORY VOC RANGES @ 60 % NV
400.00
300.00
200.00
100.00
0.00
-100.00
VOC (g/L)
20.00
25.00
30.00
35.00
39.00
% WATER


BETWEEN LABORATORY VOC RANGES @ 70 % NV
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-100.00
VOC (g/L)
10.00
15.00
20.00
25.00
29.00
% WATER

PRECISION VOC
TASK GROUP 24, SUBCOMMITTEE DO1.21
RR#1
JUNE 18, 1990

	RESULTS	ACCEPTABLE VALUES
D1475-DENSITY		
REPEATABILITY	0.40%	0.6%
REPRODUCIBILITY	3.12%	1.8%
D2369-VOLATILES		
REPEATABILITY	1.45%	1.5%
REPRODUCIBILITY	3.43%	4.7%
D3792-WATER BY GC		
REPEATABILITY	1.57%	2.9%
REPRODUCIBILITY	7.78%	7.5%
D4017-WATER BY KF		
REPEATABILITY	2.39%	4.7%
REPRODUCIBILITY	5.00%	15.0%

Precision VOC (RR#1)
Task Group 24, Sub D01.21

June 18, 1990

	Minus Water		Plus Water	
	Std Dev	Coef Var	Std Dev	Coef Var
Sample 1				
Duplicates	0.044	1.42	0.009	0.14
Repeatability	0.044	1.44	0.013	0.20
Reproducibility	0.099	3.23	0.039	0.62
Sample 2				
Duplicates	0.131	9.43	0.007	0.09
Repeatability	0.070	5.05	0.008	0.11
Reproducibility	0.328	23.58	0.024	0.34
Sample 3				
Duplicates	0.079	3.04	0.007	0.09
Repeatability	0.090	3.45	0.014	0.19
Reproducibility	0.737	28.30	0.122	1.70
Sample 4				
Duplicates	0.051	1.23	0.004	0.06
Repeatability	0.140	3.40	0.013	0.18
Reproducibility	0.328	7.98	0.101	1.41

Summary of Precision

	Minus Water		Plus Water	
	Std Dev	Coef Var	Std Dev	Coef Var
Duplicates	14.55	5.11	0.28	0.1
Repeatability	10.65	3.63	0.51	0.18
Reproducibility	54.35	18.36	3.45	1.2

AS THE VOCs GO LOWER AND LOWER:

ELIMINATE THE "MINUS WATER" CONCEPT FOR THOSE PAINTS AND COATINGS CONTAINING ONE POUND OR LESS OF VOCs

REPORT STRAIGHT VOC CONTENT WITHOUT SUBTRACTING OUT THE WATER

WHY NOT RUN VOC DIRECTLY?

ELIMINATE ALL THE VOC TESTS IN USE

THIS IS WHAT ASTM SUBCOMMITTEE D-1.21

IS EVALUATING:

ASTM TASK GROUP D-1.21.27B NEW APPROACH TO DETERMINE VOC: CHAIRMAN R. K. M. JAYANTY

⇒THIS EPA FINANCED METHOD IS AN ATTEMPT TO DETERMINE VOCs DIRECTLY.

⇒IN SUMMARY, A SEALED GLASS APPARATUS. INTO WHICH THE PAINT SPECIMEN HAS BEEN PLACED AND THROUGH WHICH DRY NITROGEN GAS IS PASSED, IS PUT INTO AN OVEN AND HEATED FOR ONE HOUR AT 100° C. THE EFFLUENTS ARE COLLECTED IN 2 CHARCOAL FILLED TUBES IN TANDEM, A 3RD AND 4TH TUBE CONTAINING INDICATING DRIERITE ARE USED TO COLLECT THE MOISTURE/WATER.

⇒BY DIRECTLY WEIGHING THE GAIN IN WEIGHT OF THE TUBES AND THE LOSS OF VOLATILES IN THE PAINT SPECIMEN, THE AMOUNT OF VOC AND WATER PRESENT CAN BE DETERMINED.

⇒IT WAS HOPED THIS DIRECT METHOD WOULD MINIMIZE THE INHERENT CALCULATION ERRORS IN REPORTING VOC AS SPECIFIED IN US-EPA's REFERENCE METHOD 24.

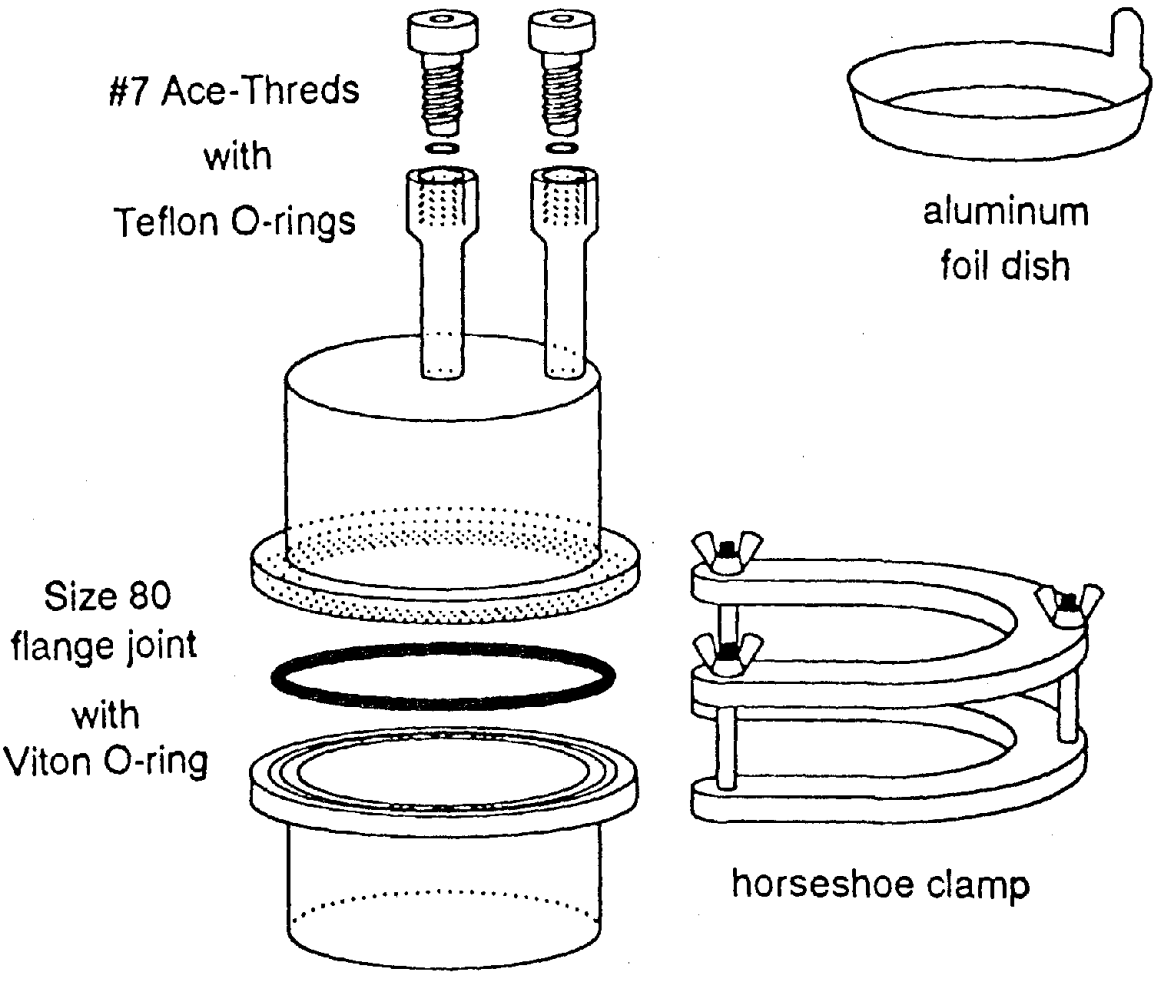


FIGURE 1. VOLATILIZATION CHAMBER

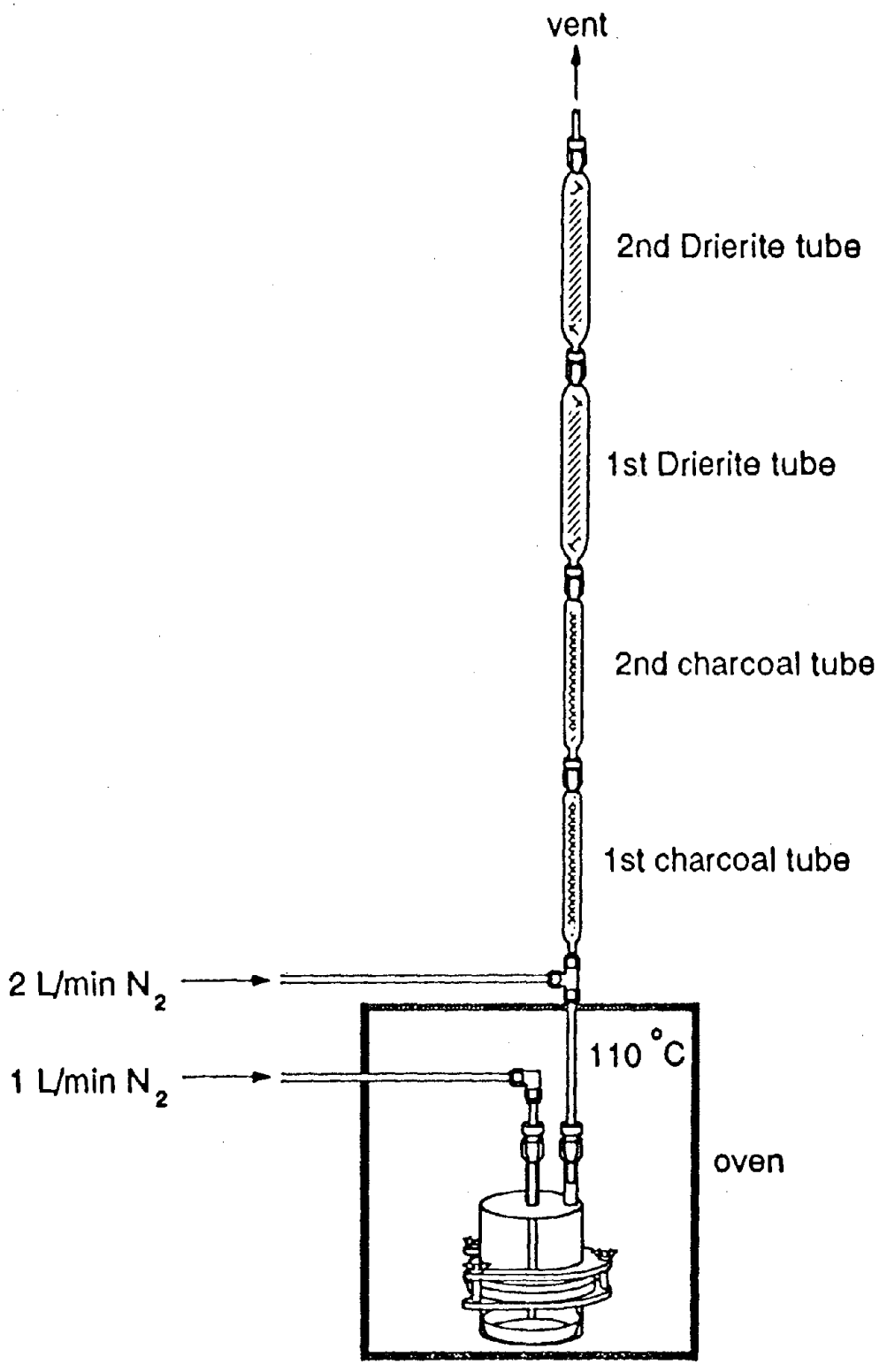


FIGURE 3. ASSEMBLED APPARATUS

⇒THE DIRECT METHOD TO DETERMINE VOCs WAS SUBMITTED FOR ASTM MAIN COMMITTEE LETTER BALLOT.

⇒THE METHOD WAS WITHDRAWN WHEN IT RECEIVED 9 NEGATIVES AND 6 COMMENTS.

⇒MOST NEGATIVES WERE DIRECTED AT THE POOR PRECISION OF 43% REPEATABILITY AND 53% REPRODUCIBILITY BETWEEN LABORATORIES.

⇒IN SUMMARY, OBJECTIONS WERE:

- APPARATUS WAS NOT COMMERCIALLY AVAILABLE
- THE APPARATUS NEEDED IMPROVEMENT, ESPECIALLY FOR LEAK CHECK PRIOR TO RUNNING THE TEST
- THE METHOD WAS TOO SLOW AND ONLY ONE SAMPLE COULD BE RUN AT A TIME
- THE CHARCOAL TUBES USED DID NOT ABSORB METHANOL AND OTHER LOW MOLECULAR WEIGHT ALCOHOLS
- THE REPRODUCIBILITY OF 53% WAS NO IMPROVEMENT OVER PRESENT METHODS IN USE

⇒THE APPARATUS HAS BEEN IMPROVED. A ROUND ROBIN IS UNDERWAY WHICH IS BEING SPONSORED BY AND RUN BY THE EPA

THE MEASUREMENTS OF HAZARDOUS AIR POLLUTANTS (HAPs)

UNDER TITLE III (HAPs MAXIMUM CONTROL TECHNOLOGY) AND TITLE V (OPERATING PERMIT PROGRAM) OF THE CLEAN AIR ACT AMENDMENTS OF 1990, SECTION 112, WE HAVE A NATIONWIDE SYSTEM OF OPERATING PERMITS FOR MAJOR SOURCES OF VOCs AND HAPs.

WE HAVE THE LEGISLATION. HOW ABOUT AN ACCURATE TEST METHOD TO MEASURE HAPs?

METHOD XXX - ANALYSIS OF HAZARDOUS AIR POLLUTANT COMPOUNDS IN PAINTS AND COATINGS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH (NOW RULE 311)

⇒ PUBLISHED ON MAY 3, 1994, RECEIVED JUNE 28, 1994 FOR COMMENTS BY US-EPA, GARY McALISTER.

⇒ THE GAS CHROMATOGRAPHIC (GC) TECHNIQUES USED ARE OUTDATED--USE OF PACKED COLUMNS AND USE OF THERMAL DETECTORS.

⇒ EXPERIMENTAL PARAMETERS ARE NOT SPELLED OUT SUCH AS INJECTION PORT TEMPERATURE, COLUMN TEMPERATURE.

⇒ UNDER THESE CONDITIONS, EVERYONE COULD DEVELOP THEIR OWN TECHNIQUES AND WHICH WOULD BE THE CORRECT ONE?

⇒ UNFORTUNATELY, VERY FEW MIXTURES CAN BE COMPLETELY SEPARATED BY GC.

⇒ RECOGNITION OF KNOWNS ARE BASED ONLY ON RELATIVE ELUTION TIME.

⇒ THE PURITY OF EACH PEAK AND OVERLAPPING PEAKS CANNOT BE DETERMINED WITH GC.

⇒ THE IDENTIFICATION OF BAKING OR CURING BY-PRODUCTS, DEGRADATION COMPOUNDS, VOLATILE OLIGOMERS, ETC. WOULD BE DIFFICULT, IF NOT IMPOSSIBLE, TO ACCOMPLISH WITH A GC.

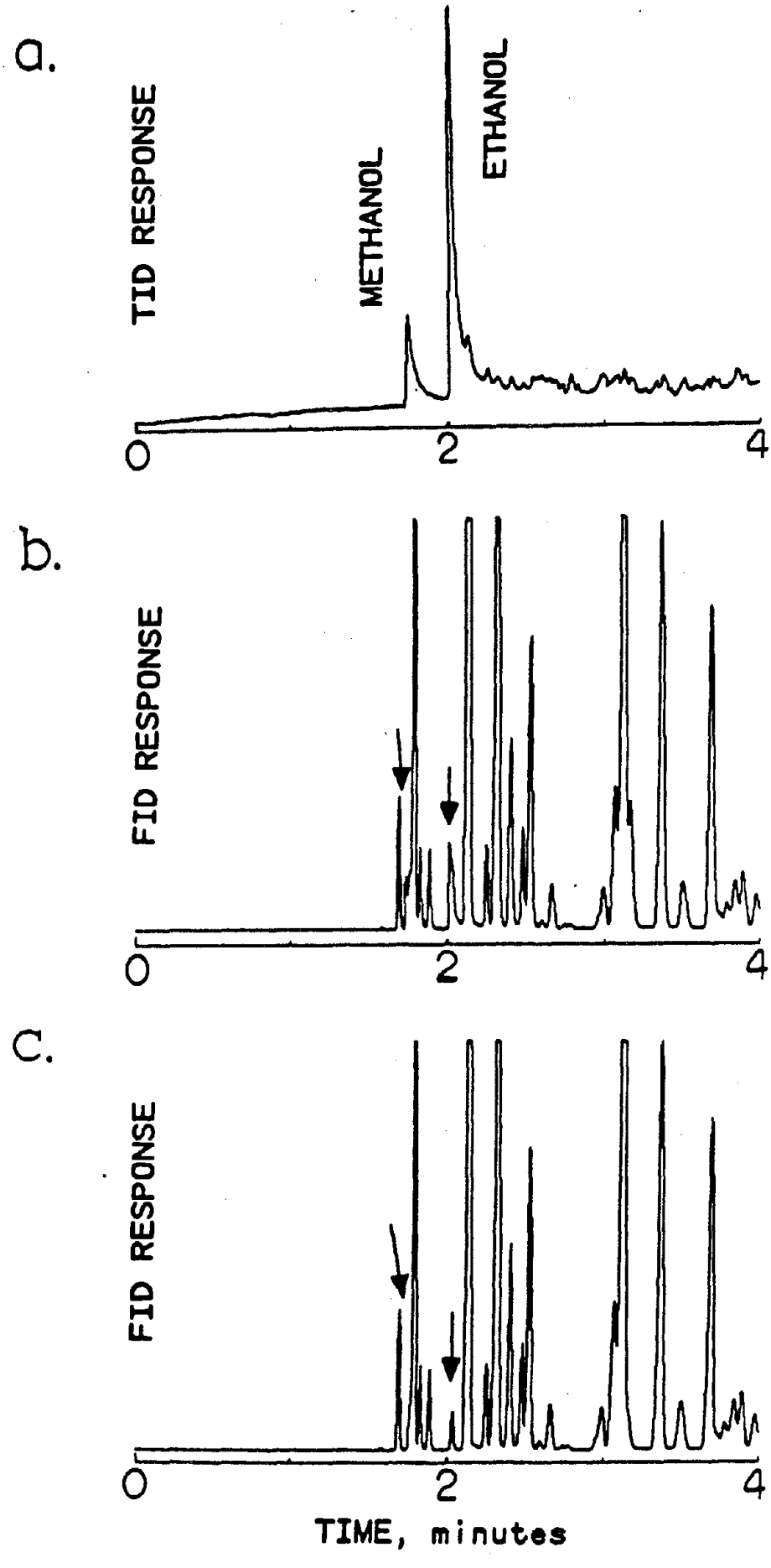
HAP's BY GC (CONTINUED)

⇒ CALIBRATION WITH STANDARDS IN THIS METHOD WOULD TAKE ALL DAY. MIXTURES OF STANDARDS SHOULD BE USED.

⇒ DILUTED PAINT SPECIMENS ARE INJECTED DIRECTLY INTO THE GC. THE MINIMUM INJECTION PORT TEMPERATURE WHICH CAN BE USED AND WHICH CAN GIVE ACCEPTABLE SEPARATED PEAKS IS 250° C.

⇒ IN RM 24, THE BAKING OR HEATING TEMPERATURE IS 110° C. ARE THE EFFLUENTS THE SAME AT 250° C AS THOSE GIVEN OFF AT 110° C?

⇒ GC WITH A HFID WOULD WORK FOR KNOWNS, BUT IT COULD NOT IDENTIFY THE CURE BY-PRODUCTS WHICH COULD CONTAIN HAPs.

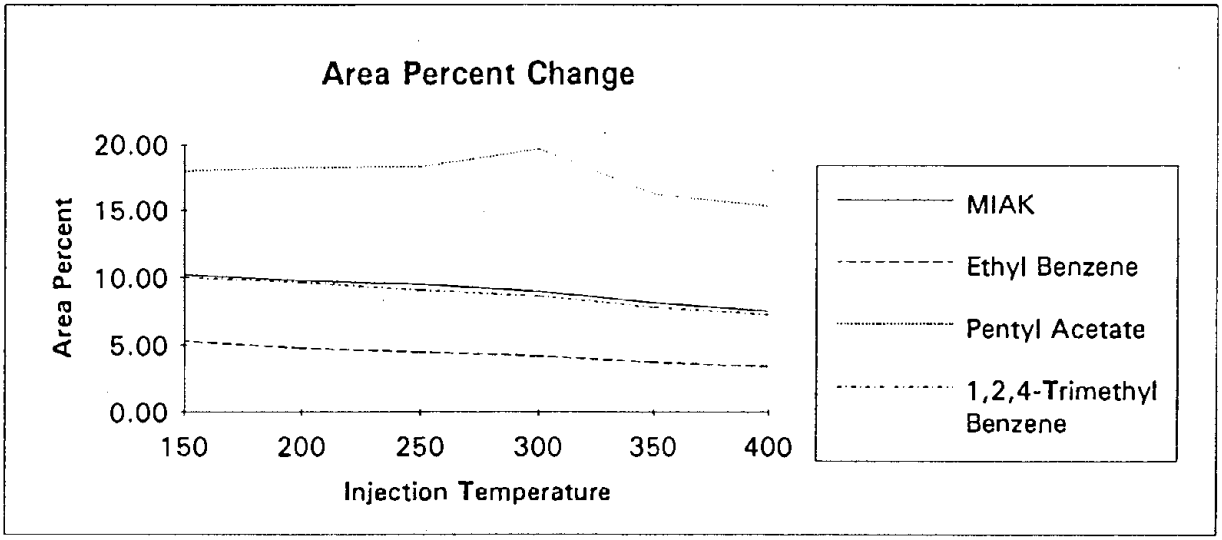

a.
TID RESPONSE
METHANOL
ETHANOL
0
2
4
b.
FID RESPONSE
0
2
4
c.
FID RESPONSE
0
2
4
TIME, minutes

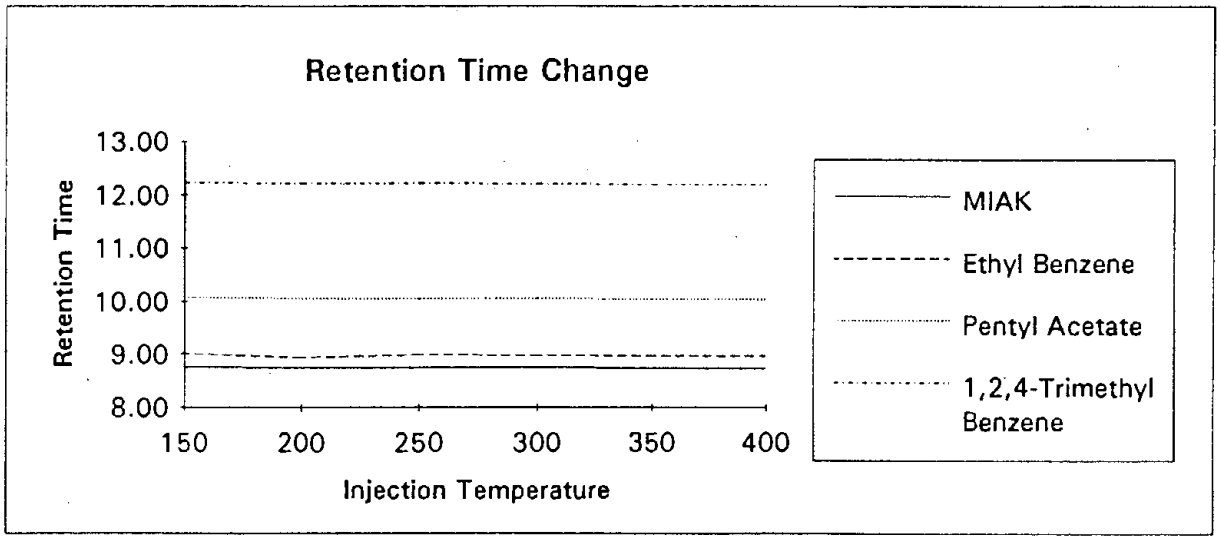
Area Percent
Injection Port Temperature

	150	200	250	300	350	400
MIAK	10.18	9.76	9.46	8.97	8.13	7.53
Ethyl Benzene	5.29	4.77	4.48	4.21	3.72	3.43
Pentyl Acetate	18.05	18.30	18.36	19.70	16.23	15.33
1,2,4-Trimethyl Benzene	10.02	9.61	9.05	8.62	7.82	7.27

Retention Time
Injection Port Temperature

	150	200	250	300	350	400
MIAK	8.75	8.73	8.74	8.73	8.72	8.72
Ethyl Benzene	9.00	8.93	8.98	8.97	8.96	8.96
Pentyl Acetate	10.07	10.05	10.05	10.05	10.04	10.04
1,2,4-Trimethyl Benzene	12.23	12.21	12.21	12.20	12.19	12.19





THE PROBLEMS WITH IDENTIFYING HAPs

⇒ GARY McALISTER, US-EPA, STATED HE WANTED ALL OF THE HAPs PRESENT IN A PAINT TO BE MEASURED AND REPORTED.

⇒ UNLESS HAPs ARE MEASURED UNDER SPECIFIED TEST CONDITIONS, CHAOS WILL REIGN.

⇒ COMPROMISED TEST PARAMETERS SHOULD BE AGREED UPON SO THAT-----HAPs IS A NUMBER OBTAINED UNDER SPECIFIED TEST CONDITIONS.

⇒ WHAT CONCENTRATION OF HAPs MUST BE REPORTED, I.E. 1.0%, 0.10%,0.010% OR 1 PPM?

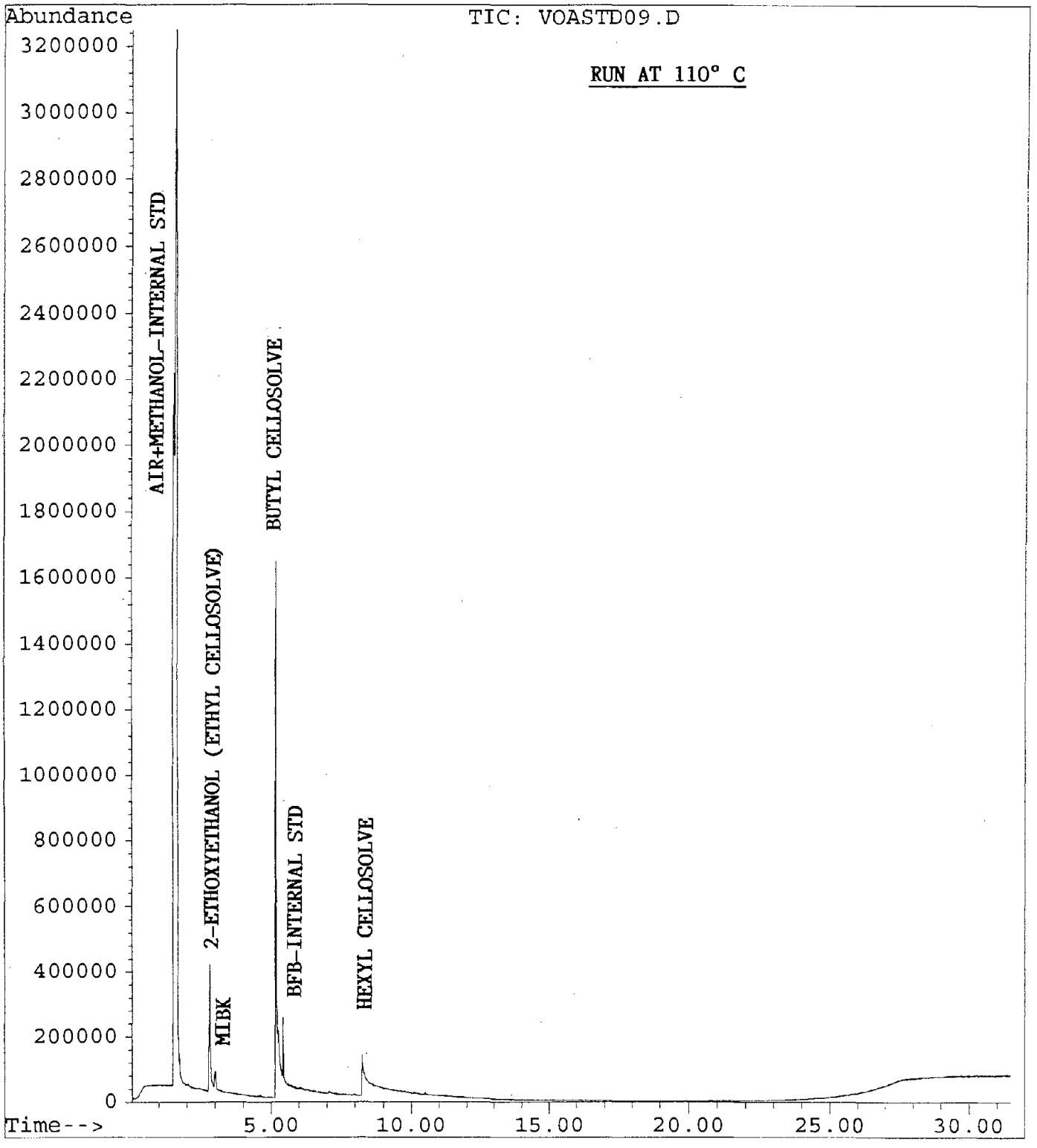
⇒ DO WE MEASURE THE HAPs EMITTED AT 110° C, THE TEMPERATURE SPECIFIED IN ASTM D 2369 "VOLATILES IN PAINTS?"

⇒ DO WE MEASURE THE HAPs EMITTED AT THE BAKING TEMPERATURE FOR THE PAINT?

⇒ SHOULD SOME COMPROMISE TEMPERATURE SUCH AS 150° C BE USED FOR MEASURING HAPs EMITTED DURING THE BAKE OR CURE?

⇒ SHOULD POWDER COATINGS BE TESTED AT 190° C?

File : C:\HPCHEM\1\DATA\950116\VOASTD09.D
Operator :
Acquired : 17 Jan 95 12:12 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: INSD+ SAMPLE E
Misc Info : 5 UL INSD +0.0221 G E
Vial Number: 10



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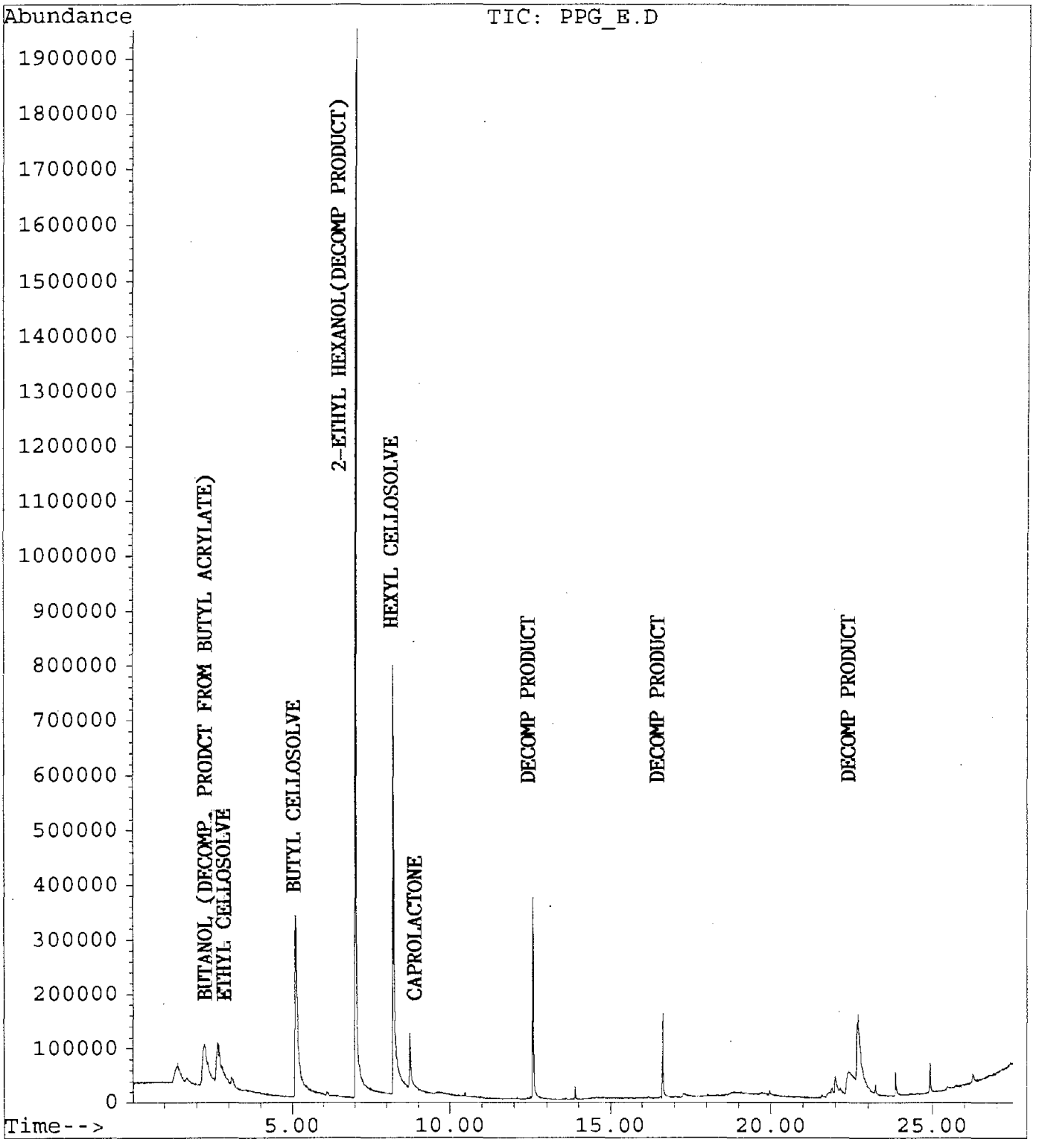
Operator : SR
Acquired : 27 Feb 95 5:53 pm using AcqMethod DIRECTSR
Instrument : 5972 - In
Sample Name: paint sample E
Misc Info : Direct injection at 250C, 45 C->300 C @10C/M
Vial Number: 1



IF SOPHISTIC HAP RESULTS ARE REQUIRED, WE MUST USE SOPHISTICATED INSTRUMENTS.

IT IS RECOMMENDED THAT:

⇒ **A METHOD USING HEADSPACE/GAS CHROMATOGRAPHY/ MASS DETECTOR BE DEVELOPED,**

⇒ **WHICH USES SPECIFIED TEST CONDITIONS,**

⇒ **TO IDENTIFY AND TO QUANTITATE HAPs PRESENT IN PAINTS AND COATINGS!**

SUMMARY OF THE HS/GC/MS TECHNIQUE

FOR HAPs

⇒ A 20 MG PAINT SPECIMEN IS WEIGHED INTO A 20 mL HEADSPACE VIAL AND SEALED. INTERNAL STDS CAN BE WEIGHED IN AT THE SAME TIME

⇒ THE VIAL IS HEATED AT 110° C IN THE HEADSPACE FOR 20 MINUTES

⇒ A 3 mL ALIQUOT OF THE HEAD-SPACE IS INJECTED INTO A 30 m FUSED DB-5 CAPILLARY COLUMN

⇒ CHROMATOGRAPH TEST PARAMETERS:

- INJECTION MODE = SPLITLESS FOR INITIAL 30 SECONDS
- INITIAL OVEN TEMPERATURE = 45° C (FOR 1 MIN.)
- PROGRAM RATE 10° C/MIN.
- FINAL TEMPERATURE = 300° C (HOLD FOR 5 MIN.)

⇒ THE SAMPLED MIXTURE OF VOLATILES ARE CHROMATOGRAPHED AND THE ELUTING PEAKS IDENTIFIED BY THEIR UNIQUE MASS SPECTRA.

⇒ RELATIVE RESPONSE RATIOS (RRRs) WITH RESPECT TO A SPIKED INTERNAL STANDARD ARE USED TO DETERMINE THE QUANTITY OF EACH COMPOUND FROM THEIR PEAK AREAS.

WITH THE USE OF THE HEADSPACE

⇒ WATER OR SOLVENT-REDUCIBLE WET PAINTS CAN BE TESTED

⇒ POWDER COATINGS CAN BE RUN

⇒ MULTI-COMPONENT PAINTS, WET OR CURED, CAN BE RUN

⇒ VARIOUS HEATING TEMPERATURE PARAMETERS CAN BE USED WITHOUT DISTORTING THE CHROMATOGRAMS

⇒ INTERNAL STANDARDS TO QUANTIFY RESULTS CAN BE USED

⇒ THE USE OF VERY SMALL SAMPLE SIZE DECREASES THE EFFECTS OF THE PARTITION COEFFICIENT IN HEAD-SPACE ANALYSIS

WITH THE GC/MS

⇒ MOST ELUTED PEAKS CAN BE IDENTIFIED QUICKLY

⇒ OVERLAPPING PEAKS CAN BE IDENTIFIED

⇒ THE PURITY OF THE PEAKS CAN BE CHECKED

⇒ ALL THE HAPs PRESENT IN THE CHROMATOGRAM CAN BE FLAGGED

⇒ UNKNOWNS CAN BE RUN AND THE ELUTED PEAKS OF HAPs CAN BE IDENTIFIED

⇒ USE OF INTERNAL STANDARDS HAS THE POTENTIAL TO GIVE GOOD QUANTITATIVE RESULTS

SOME OF THE DRAWBACKS USING HS/GC/MS

⇒ COST OF THE INSTRUMENT- -$40K TO $100K

⇒ NEED TO DECREASE THE EFFECT OF THE PARTITION CO-EFFICIENT BY USE OF SMALL SAMPLE SIZE

⇒ MATRIX EFFECT

⇒ DETERMINATION OF RELATIVE RESPONSE RATIOs(RRRs). CAN GENERIC STANDARDS BE USED?

⇒ NEED FOR MORE RESEARCH

⇒ REQUIRES STRONG BACKGROUND IN ORGANIC CHEM-ISTRY

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Operator : SR
Acquired : 5 Nov 94 12:38 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: WATER BASED ADHESIVE
Misc Info :
Vial Number: 8

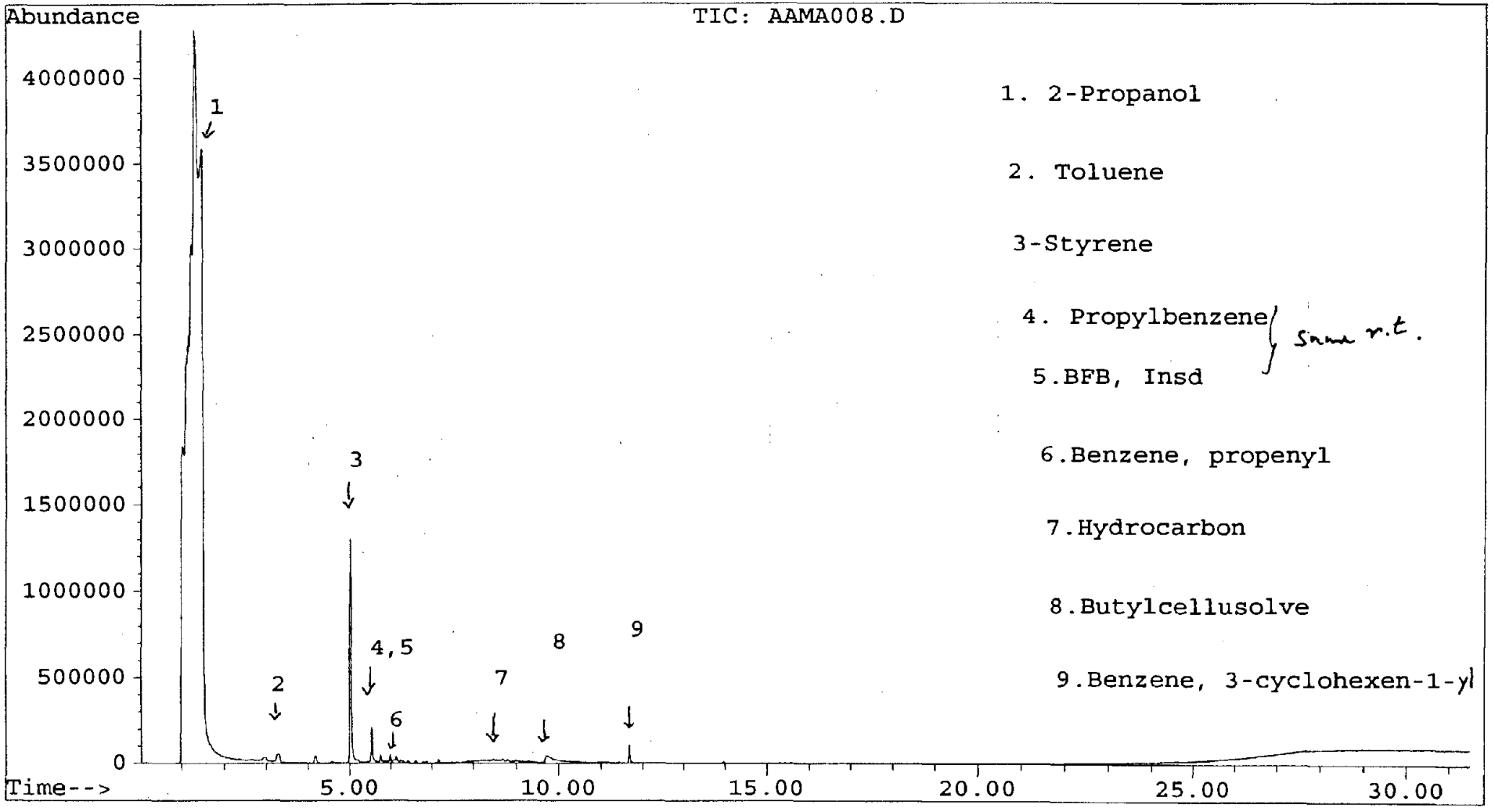
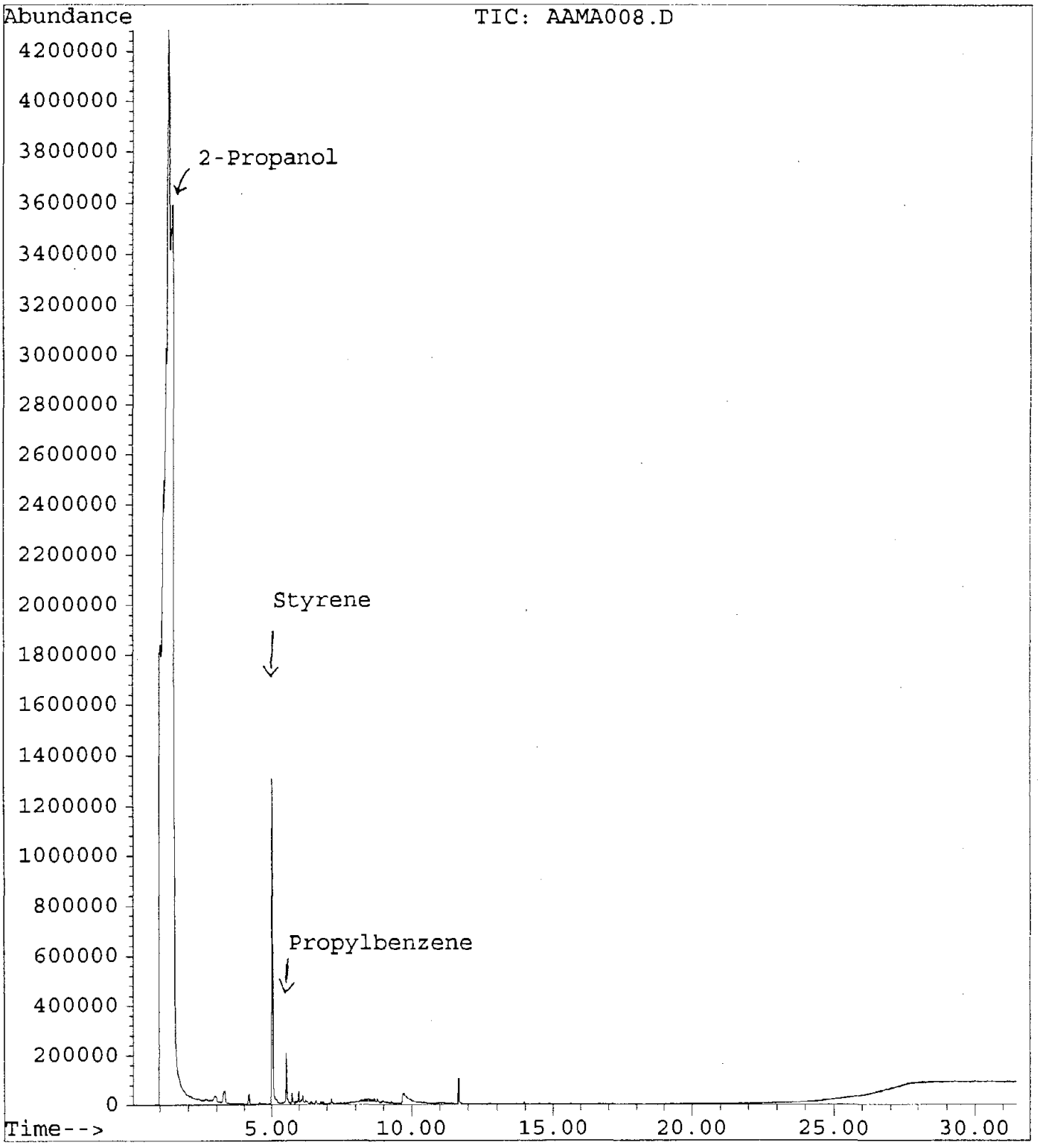


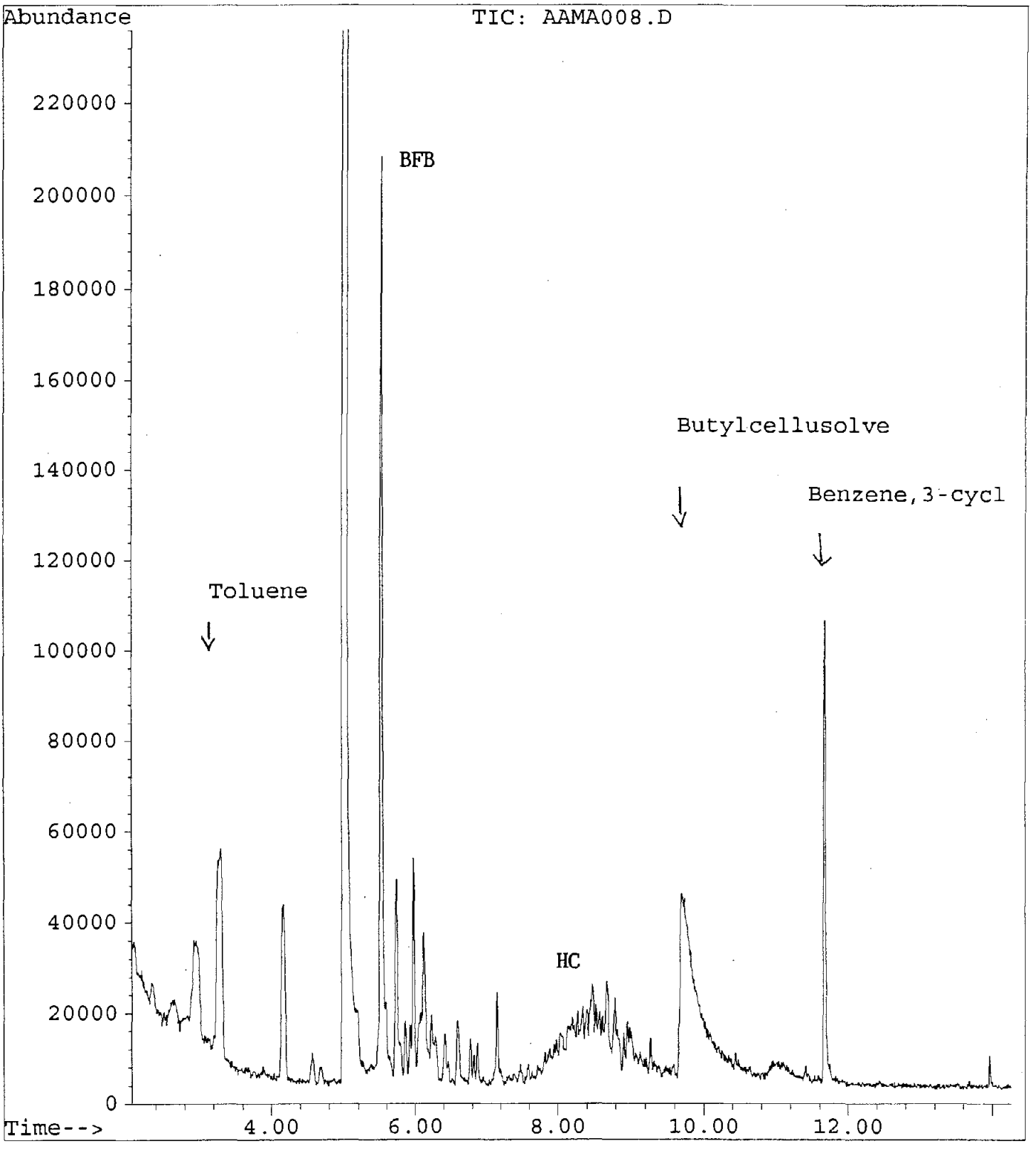
Table 19

TIC:	008.D								
		HC-7111 Water Based Adhesive,							
	Peak #	Time	Area	ID			ppm		
	1	1.502	2.29E+08	2-propanol			21360.52		
	2	2.961	1527991	2-pentanone, 4-methyl-			14.26125		
	3	3.301	2329247	**Toluene**			21.73964		
	4	4.173	1456328	Cyclohexene, 4-ethenyl-			13.59239		
	5	5.024	39172094	**Styrene**			365.6062		
	6	5.523	1000000	**Propylbenzene**			9.333333		
	7	5.523	3000000	BFB, insd		27.98769			
	8	5.738	1161053	cyclohexane, diethyl-			10.83649		
	9	5.863	306116	**Benzene, 1-propenyl-**			2.857083		
	10	5.98	1272977	**Benzene, propyl-**			11.88112		
	11	6.123	1121264	benzaldehyde			10.46513		
	12	6.878	428592	**Benzene, 1-methyl-2-propyl-**			4.000192		
	13	8.678	7868964	hydrocarbons			73.44366		
	14	9.7	6901277	**Ethanol, 2-(2-butoxyethoxy)-**			644.1192		
	15	11.678	1808534	**Benzene, 3-cyclohexen-1-yl-**			16.87965		
						total=	22559.53	%	
								2.255953	
						US EPA RM-24		0%	
		Based on RM-24, we reported no VOC. However, our HS GC/MS shows the presence of							
		the above.							
		The compounds flagged (BOLD) are HAPs.							
		The MSDS sheet mentioned only formaldehyde-melamine polymer @ >60%.							
		From the compounds detected, there seems to be Styrene:Butadiene latex compounds.							

File : C:\HPCHEM\1\DATA\941104\AAMA008.D
Operator : SR
Acquired : 5 Nov 94 12:38 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: #18
Misc Info : #18, 0.3573g
Vial Number: 8



File : C:\HPCHEM\1\DATA\941104\AAMA008.D
Operator : SR
Acquired : 5 Nov 94 12:38 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: #18
Misc Info : #18, 0.3573g
Vial Number: 8



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	12	6.878	428592	**Benzene, 1-methyl-2-propyl-**			4.000192			
	13	8.678	7868964	hydrocarbons			73.44366			
	14	9.7	6901277	**Ethanol, 2-(2-butoxyethoxy)-**			644.1192			
	15	11.678	1808534	**Benzene, 3-cyclohexen-1-yl-**			16.87965			
						total=	22559.53	%		
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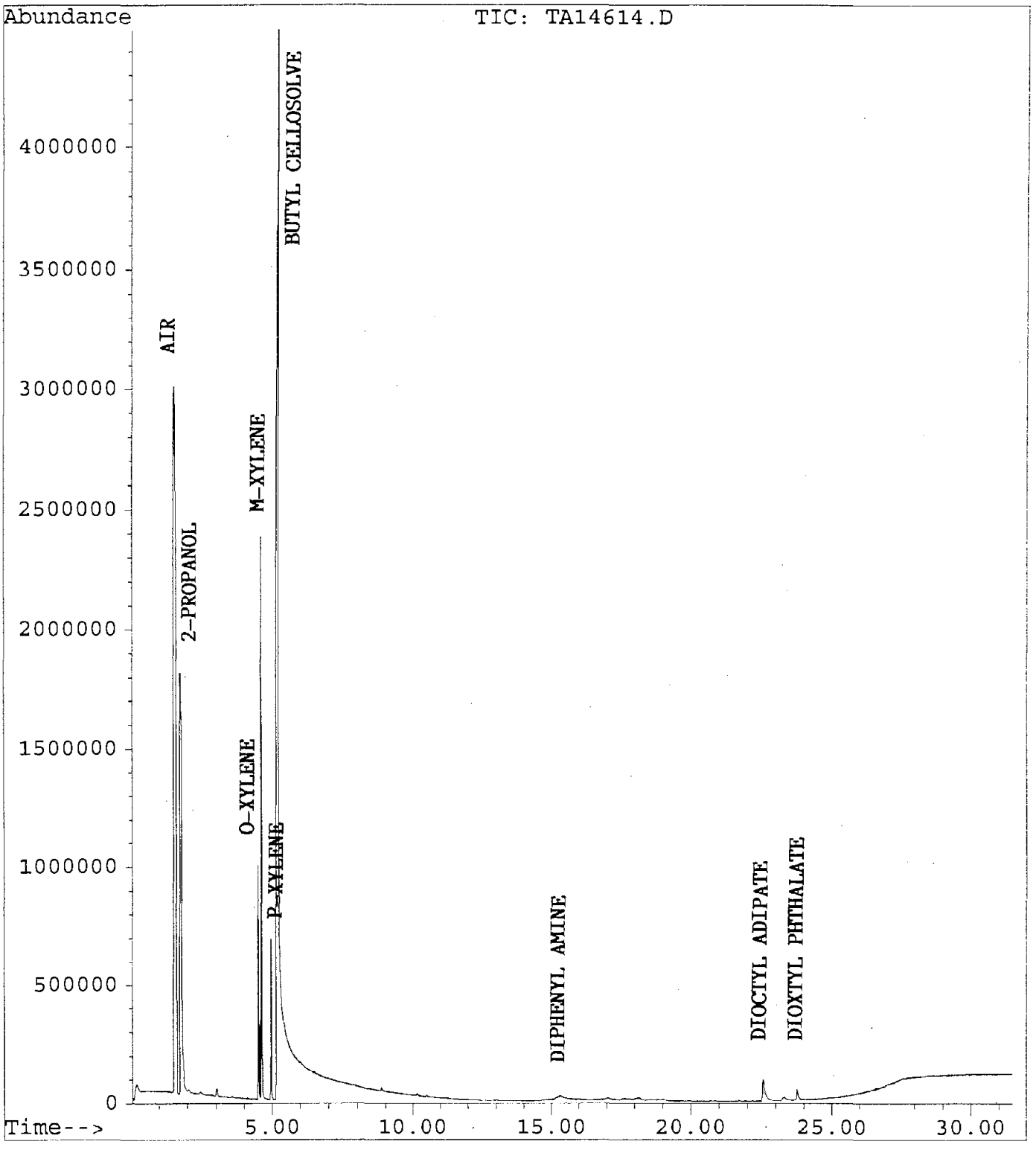
		Based on RM-24, we reported no VOC. However, our HS GC/MS shows the presence of								
		the above.								
		The compounds flagged (BOLD) are HAPs.								
		The MSDS sheet mentioned only formaldehyde-melamine polymer @ >60%.								
		From the compounds detected, there seems to be Styrene:Butadiene latex compounds.								

File : C:\HPCHEM\1\DATA\TA14614.D
Operator : SR
Acquired : 2 Feb 95 11:43 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: SAMPLE TA14614.
Misc Info : HS/GC/MS
Vial Number: 1



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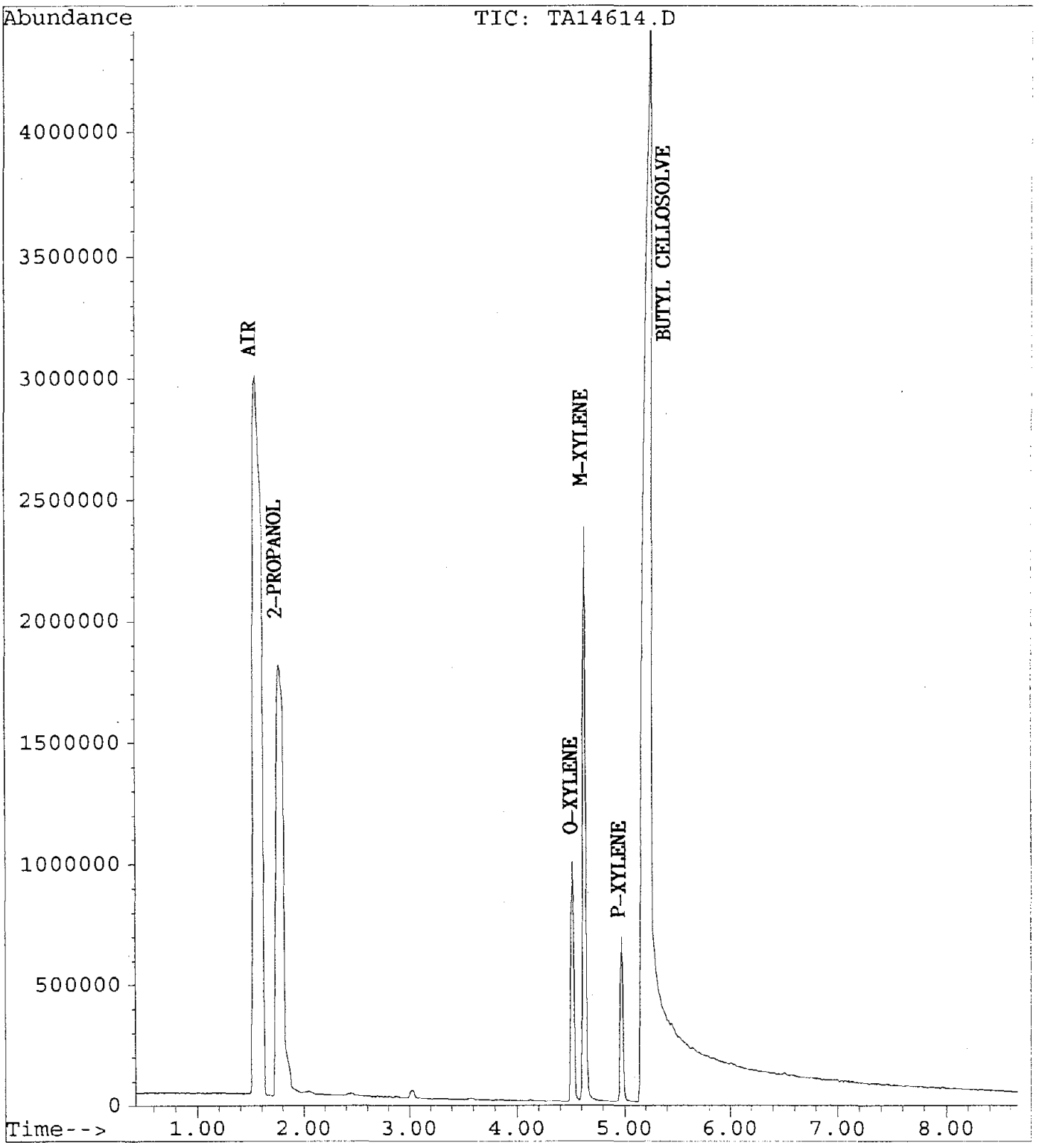
Acquired : 2 Feb 95 11:43 am using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: SAMPLE TA14614.
Misc Info : HS/GC/MS
Vial Number: 1



CONCLUSION ON ANALYSIS FOR HAPs IN PAINTS

OUR STUDIES HAVE LED US TO CONCLUDE:

⇒ **THE USE OF HS/GC/MS WILL BE A NEEDED SUPPLEMENT FOR THE VOC DETERMINATION BY US-EPA's REFERENCE METHOD 24.**

⇒ **USE OF THESE INSTRUMENTS WILL MEET THE REQUREMENTS STATED IN TITLE III AND TITLE V OF THE 1990 CAAA, THAT IS, IDENTIFICATION OF ALL THE HAPs CONTAINED IN PAINTS AND COATINGS.**

CONCLUSION (CONTINUED)

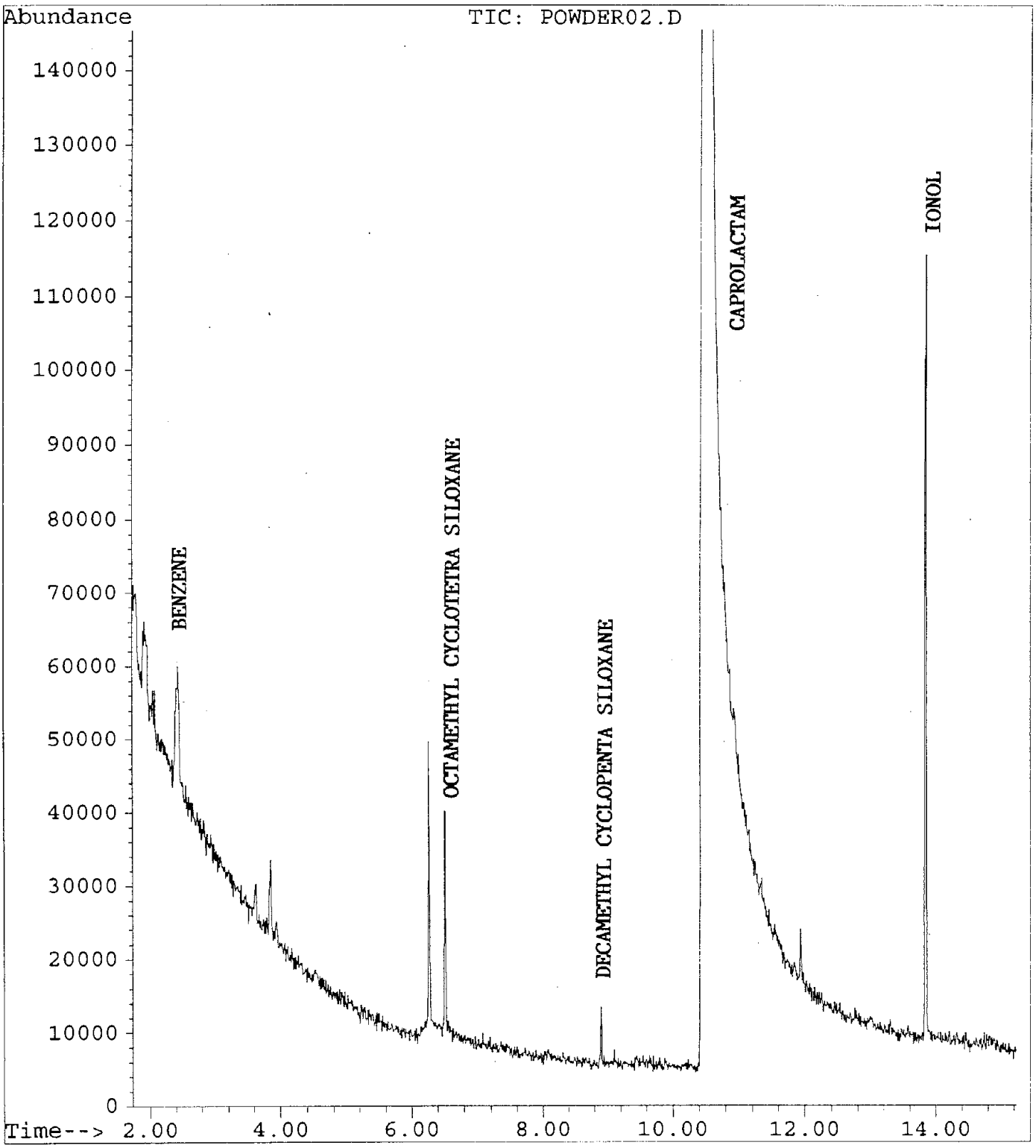
THE MOST SIGNIFICANT OBSERVATION MADE WITH THE GC/MS ANALYSES WAS:

⇒MANY OF THE PAINTS CONTAINED COMPOUNDS WHICH WERE ON THE US-EPA's 189 HAPs LIST AND WHICH WOULD NOT HAVE BEEN FLAGGED BY GC ALONE OR BY REFERRING TO THEIR MSDS SHEETS.

⇒ ALL THE COMPOUNDS LISTED ON A MSDS SHEET MAY NOT EVOLVE AT THE 110° C TEMPERATURE USED IN ASTM TEST METHOD D 2369.

⇒ SOME OF THE EFFLUENTS FOUND WERE NOT ON THE MSDS SHEET.

File : C:\HPCHEM\1\DATA\950206\POWDER02.D
Operator :
Acquired : 2 Feb 95 2:15 pm using AcqMethod RAMESHHS
Instrument : 5972 - In
Sample Name: SAMPLE G-P
Misc Info : POWDER G-P POLYESTER 0.076.2 MG
Vial Number: 3



	% VOC calculations:			Powder Coatings.			
			@110C		E-EP	@193C	
% Volatiles:			-0.8			1.3	
% water:			0			0	
Density of specimen, g/mL =			1.65			1.65	
VOC (straight) =			-13.2	grams/litre		21.45	
			-0.11	lbs/gallon		0.179	
			@110 C		G-P	@193C	
% Volatiles:			-1.03			3.6	
% water:			0			0	
Density of specimen, g/mL =			1.56			1.56	
VOC (straight) =			-16.068	g/litre		56.16	
			-0.13	lbs/gal		0.47	LBS/GAL
E-EP = Epoxy-polyester hybrid							
G-P = Polyester							

CONCLUSIONS

⇒ PAINT TECHNOLOGY IS IMPROVING DAILY WITH PAINTS AND COATINGS COMING INTO THE MARKET-PLACE WITH LOWER AND LOWER VOCs.

⇒ ALONG WITH THESE INNOVATIONS, THERE MUST BE CHANGES OR MODIFICATIONS MADE IN TEST METHODS AND IN CALCULATIONS NEEDED TO MEASURE THESE LOW VOCs.

⇒ AS THE VOC NUMBERS GET LOWER, THERE WILL BE, STATISTICALLY, GREATER VARIATION IN TEST RESULTS DUE TO THE PRECISION INHERENT IN EACH TEST METHOD USED TO MEASURE VOCs.

CONCLUSIONS (CONTINUED)

⇒ IT IS RECOMMENDED THAT WE DROP THE "MINUS WATER" CONCEPT FOR PAINT PRODUCTS WITH VOCs LOWER THAN ONE POUND.

⇒ HOW LOW A VOCs NUMBERS MUST BE OBTAINED BEFORE ONE CAN DECLARE A PAINT CONTAINS "ZERO" VOCs?

⇒ SPELL OUT IN DETAIL WHAT TEST PARAMETERS ARE TO BE USED IN DETERMINING THE HAPs PRESENT IN PAINTS AND COATINGS.

⇒ WE NEED ANSWERS: ARE THE HAPs PRESENT IN WET PAINT TO BE MEASURED AND/OR HAPs EMITTED DURING THE BAKING SCHEDULE OR BOTH?

Developments in European VOC Emission Regulations
(Into or out of a maze?)

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Teddington, Middlesex TW11 LD
United Kingdom
Tel. 44 181 977 4427
Fax. 44 181 943 4705

INTRODUCTION

Legislators and industry face the same questions in addressing pollution control:

what substance should be controlled and to what level
where to apply the controls
and how to apply controls

This paper examines how these problems have been addressed in relation to VOC emission control legislation in what is now the European Union (EU: pre Maastricht, the European Community, EC). My aim is to draw out features of the legislation thus enabling comparison of US and European approaches to the primary international environmental issue facing the coating industry: that of involvement of VOC emissions in ground level ozone formation I also aim to steer those of you whose companies operate or are contemplating operation in Europe through the legislation maze or towards specialist advice before embarking on your venture.

The European Union is not an homogeneous entity; it is not a federation, though some may wish it to be. It is a free trade grouping made up of 15 individual member States each with its own culture, language, economic performance, industrialisation, climate and indeed air quality. The variation National characteristics is a problem for European legislators, imagine trying to reach an agreement on a detailed technical proposal with even like minded individuals when at least ten different languages are involved. It will therefore be no surprise to you to learn that the approach to and details of VOC emission control legislation varies throughout the Union. Equally, some 250 EC directives and regulations relating to the environment have been issued since the first measure was adopted in 1967[1].

Against this background, the paper can only be a overview which focuses on painting processes. There is not time nor space to present complete details of each piece of legislation or the control of other VOC emission sources, which include surface cleaning and other coating processes I offer a personal view, drawing upon my experience in helping companies comply with legislation, which I hope will give a practical, balanced guide since I am a engineer without the potentially partial interests of a politician, industrialist or legislator The paper considers the legislation driving forces, the scope of existing and emerging controls in the EU, and offers some suggestions for future developments

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LEGISLATION DRIVERS
(Into The Maze)

Air Quality, the need for control

Background concentrations of ground level ozone in the Northern Hemisphere are reported[2] to have increased 2 fold over the last century and are continuing to increase at a rate of 1 to 2% per annum. High concentrations are associated with rural areas, although peaks in urban areas approach these levels (largely due to traffic emissions): the concentration of VOCs is highest in urban areas. Peak levels of 180 ppb are observed in Central Europe, while in Scandinavia they are rarely above 80 ppb; peaks in the UK are between these values. There is some evidence that ozone levels in the UK and in Holland are an imported phenomenon, underlining the transboundary nature of the problem.. However, in spite of several years of co-ordinated international measurements, there is no comprehensive picture which includes , seasonal or episodic behaviour of the ozone or VOC distributions over Europe.

Some coating related VOCs emissions are potentially toxic and odorous air pollutants. The extent to which VOCs represent a global threat to human health is unclear, as ambient air monitoring of organic compounds is in its infancy. It is notable that of the 26 organic compounds now being monitored only heptane, xylene and toluene are potentially attributable to coating industry use of solvents. While there is concern about the levels of carcinogens such as benzene and 1.3 butadiene, the VOCs resulting from solvent use in the coating industry are not seen as representing a significant health risk. Thus air quality issues related to the toxic and odorous properties of VOCs emitted from coating operations are invariably local to a specific facility.

International Protocols

VOC emissions were the subject of the 1991 Geneva Protocol under the UNECE Convention on Long Range Transboundary Air Pollution. Parties to the Protocol (USA, Canada, EC member states with the exception of Italy and Portugal, and the European Community) agreed to achieve a 30% reduction (1988 reference) in their national non- methane VOC emissions by 1999. Additional obligations under the Protocol include:

- application of emission limits based on best available technologies and economic feasibility to new mobile and stationary sources and to existing sources where ozone air quality standards are exceeded or where VOC fluxes originate.
- application of control measures to products which contain solvents and promotion of low organic solvent products
- priority action on VOCs with the greatest photochemical ozone creation potential
- substitution of toxic and ozone depleting VOCs by less harmful substances

within 5 years of introduction of the Protocol. Thus placing reduction of VOC emissions on the legislation agenda of the European Commission and member state Governments

Action under the VOC Protocol is directed towards reducing background ozone levels and is not expected to eliminate the incidence of severe ozone episodes. The frequency of episodes in Europe is such that WHO guideline concentration values are regularly exceeded thus potentially threatening human health, agriculture, materials and the environment. Additional measures to control ozone precursor emissions are thus likely to be considered in a Protocol review scheduled for 1996. Assessment of the costs and benefits of action taken to meet the existing VOC emission reduction target is likely to take some time. In its current review of the NOx Protocol under the Transboundary Convention the UNECE is considering the feasibility of producing a "Multi- Media - Multi effect" Protocol to address emissions of both VOCs and NOx in view their association in ozone formation. Conclusions on this are also not expected for some time. Thus no international calls for further curbs on VOC emissions are expected before 2000.

CONTROLS IN MEMBER STATES
(Deep In The Maze)

Strategic Approaches

Several member states have developed or are developing VOC emission reduction programmes to meet their commitments under the Geneva Protocol. Notable among these is the KWS 2000 Project conducted in the Netherlands. This project is an example of interactive policy making in which government and industry examined the options for reducing VOC emissions in order to establish effective, realistic and equitable goals. The project involved national and local government (responsible for issuing permits) and industry representatives. Pressure groups and consumer groups were consulted but not formally involved in the process. The project concluded with the publication of a control strategy[3] based on reduction of both solvent use and industrial VOC emissions: vehicle and agriculture emissions were not considered. The plan contains a programme of reduction targets for specific sources and compounds leading to the prospect of a 58% reduction (from 1981 levels) in VOC emissions by 2000. Industry involvement in the plan would seem to be beneficial since the Environment Ministry were initially seeking 50% reduction. It was envisaged that the actions to achieve the reductions would include: manufacturer initiatives, education, and government purchasing policies. A feature of the plan is a projected 50-60% reduction in emissions from painting operations following the introduction of low VOC coatings, improved application methods and non-organic surface cleaners.

The UK has developed and is implementing a reduction plan[4]. The plan, mainly regulator led with industry involvement, is based on consideration of solvent usage and the VOC emissions from industry, combustion plant, agriculture and vehicles. Implementation is largely being effected by the application of emission controls to industrial solvent users through the permitting of processes under the 1990 Environmental Protection Act. The plan is projected to produce the required 30% reduction in VOC emissions. However, there is some concern that this will be insufficient to prevent levels in some UK areas exceeding a proposed ambient air ozone standard of 50 ppb[5].

France has also undertaken a strategic review and reached formal agreements with the solvent using and coating industries in order to effect a 30% reduction in

emissions. The Danish government is currently conducting a similar strategic exercise to KWS 2000 in conjunction with the Industry Council.

Sweden achieved a 15-20 % reduction in industrial VOC emissions by 1992 as a result low cost measures such as process changes, control of fugitive emissions and the use of low solvent products. These measures are not sufficient to achieve an the intended reduction of 50% by 2000. Thus the Swedish EPA is planning to apply stricter controls to those plants already regulated and to extent controls to other activities[6].

Development of strategies has stimulated industry led initiatives to reduce VOC emissions. European coating manufacturers have developed their own policy[7]. They are suggesting [8] a progressive reduction in the solvent content of decorative, architectural and some professional (vehicle refinish) paints be stimulated through a compulsory Eco-Labelling scheme. They have suggested the solvent levels which might be used as a label award criterion. Clearly, there is merit in industry participation in the development and implementation of emission reduction plans

The industry sectors and processes subject to VOC emission control are commonly selected using emission inventories based solvent input rather than actual organic compound emissions. Such inventories may intrinsically overestimate source emissions because paint usually contains a mixture of impure solvents of variable volatility and solvents enter other waste streams. The inventories, nor controls based on total hydrocarbon emissions, take no account of photochemical ozone creation potential variations between VOCs (although this distinction only applies if ozone formation is the only adverse impact). They also create a problem solvent definition for the purpose of VOC emission control. The UK regulations contain some 4 definitions, EC regulations another: recent publication of a CEN definition may be helpful. All VOC definitions encompass the coating degradation product emissions from stoving plant which are also not accounted in inventories. The problems are only partially overcome when solvent mass balance data is used to compile inventories. Clearly, effective focusing controls will only follow from inventories based on measurement.

Ozone formation and organic solvent use have become synonymous to extent that restriction in paint solvent content is considered the most economic way of reducing the environmental impact of paint and painting. This is may be so in the case of architectural / decorative and certain commercial (vehicle refinish) painting . However, this approach can lead to reductions in coating performance, often neglects creation of other impacts (such as odour) and the costs associated with re-equipment, production re-scheduling and energy consumption created by introduction of , say, a waterborne coating. Recent paint life cycle inventories have shown that significant environmental impacts can arise from raw material production and paint stoving. The energy used in waterborne paint stoving is greater than that for an equivalent organic solvent based system. The overall impacts of solvent and water based paints are comparable and inversely related to coating life. These factors has led to an industry view that there is too much emphasis on VOC emissions as a separate issue and that it is time for legislators to focus on "greatest" environmental risks in controlling paint and painting processes.

Industrial Emission Controls

Plant permitting is commonly used throughout the Union as a basic method of applying legal controls to industrial operations. As a result of EC directive 84/360 member states have in place a system of permitting major polluting facilities in the energy, chemical, mineral metallurgical and waste industries. Coating industry permitting and associated pollution control may be effected through environmental protection, planning, public health, worker safety, nuisance or common(case) law. Although the laws may be international (EU regulations), the current regulations relating to the coating industry and VOC emissions are national or regional. Such control can, while allowing flexibility in matching emission control requirements to local economic and environmental circumstances, can lead to a number of problems:

- neglect of emissions to atmosphere (if the local body is primarily responsible for planning, waste or water issues)
- focus on local nuisance issues (odour, noise, visual impact, amenity)
- focus on specific pollutants (smoke)
- neglect of transboundary effects of emissions
- wide variation in emission control requirements
- variation cost of control for a particular type of operation

Clearly, this last problem is of great concern to the coating plant operators in respect of their competitiveness when their operation is located in an area with tight emission controls. Thus there is a case for national or international statutory emission limits or guidance.

Emission Standards

Legislation relating to coating operations and VOC emission control is highly variable throughout the Union. Only in a few member states has National legislation or guidance relating to VOC emissions limitation been established. These tend to be the northern industrialised nations, leading to concerns in these countries about competitiveness and in the others fears of possible importation of pollution as a result of industry migration.

In several states VOCs are controlled by applying National emission concentration standards for particular compounds across the industrial spectrum: coating operations may be specifically addressed. For example, Germany, Italy and Denmark have a comprehensive listing of individual organic compounds subject to control. The emission limit applied is based on substance toxicity categorisation with the lowest being applied to carcinogenic material. The limits become applicable when the substance mass emission exceeds a given level. The emission standard for a particular compound and the threshold at which it becomes applicable vary from country to country.

In other states National VOC emission standards are applied to specific industrial operations: these can be substance and coating operation specific. This the case in France where the coil and vehicle coating industries are subject to control. France is also probably unique in controlling VOC emissions (in vehicle manufacture) by applying percentage reduction requirements rather than concentration limits.

The UK probably has the most comprehensive and sophisticated legislation on VOC emissions from coating processes. The Environmental Protection Act of 1990 established a new national pollution control regime based on scheduled processes and

substances releases (to all media) which brought coating processes under specific control for the first time. The list of scheduled coating and printing processes subject to local control under national guidance includes: coating of metal and plastic, metal packaging, coil, drums, road vehicles, aircraft, railcars, wood, vehicle respraying and includes coating manufacture. Both new and existing processes are subject to permitting and emission limits if the total solvent input exceeds 5 tonnes per annum (1 tonne in the case of vehicle refinish and 100 tonne for coating manufacture). The substances subject to emission limits are specific to the coating operation. The concentration emission limits applicable to new plant reflect the human and environmental hazards of the substance emitted (isocyanate, 0.1 mg/m^3; chlorinated hydrocarbons 20 mg/m^3; total hydrocarbon 50 mg/m^3) and depend on the mass emission and the operation (spraying, stoving oven). Exemptions apply if low VOC coatings are employed. The VOC levels in "compliant coatings" vary with industry sector, substrate and coating type (primer, base coat, top coat, two pack) but are in the range 250 to 850 g/l and are typically about 400 g/l excluding water. Existing plant must be upgrade to the new plant standards between 1995 and 2000, depending on the process. Conditions contained in an operating permit are legally enforceable. As well as emission limits these include obligations on plant operation and housekeeping, emission monitoring, dispersion and a general requirement to minimise and render harmless releases to the environment.

Where a specific coating operation is subject to limits or guidance, the solvent use or emission threshold bringing the operation into the control regime, the substances and process elements subject to control and the VOC emission limit applied can vary between countries.

For all states where national emission standards are in place the concentration limit values reflect the levels achievable by employing best available techniques. Individual substances subject to control are selected on the basis of human, rather than environmental, toxicity. Some chlorinated hydrocarbons are controlled for environmental reasons. POCP is not used as the basis for ranking organic compounds for the purposes of applying differential limits The UK's approach of controlling VOCs by applying a blanket total hydrocarbon emission limit is particularly vulnerable to criticism for this reason, though it does have the advantage of simplifying emission measurement.

Other control measures

Emission limits applied to factory based coating don't address significant VOC releases from decorative, architectural and maintenance paints (e.g. decorative paints contribute 4-6% to total VOC emissions). The measures addressed in the following are more appropriate for control of such releases and may well have a role in industrial emission control.

Product Controls

These may derive from specific regulations relating to the content of preparations or from product standards. Legislation is in place throughout the community to control the dangerous substances content of consumer and trade goods (for example the legislation following EEC directive 76/769 Restrictions on Marketing and Use of

Certain Substances prohibits vinyl chloride monomer and asbestos in paints and restricts cadmium uses) and to ensure product safety (e.g. toy coatings and adhesives). Product standards are also used to control the lead and sulphur in fuel for environmental purposes.

Use of product standards for VOC emission control is limited to a number of States. Denmark has in place a prohibition of organic solvent in DIY and professional decorative and maintenance paints. Austria has legislation limiting the solvent content of decorative paints to 10% from 1996.

Economic Instruments:

Economic instruments include tradable emission permits, taxation (on raw materials, emissions or on products) and subsidies (grants, preferential loans). European legislation provides for use of these measures but subsidies may be considered to violate the "polluter pays principle". Their use for emission control is not widespread: there is some limited use of preferential loans for pollution control projects in Germany. With the possible exception of fuel and liquors, their use in relation to VOC emission control is minimal: Luxembourg subsidises production of waterbased paints. Nevertheless their application is being examined in several member states[9]. They are an increasingly favoured measure in the UK and the DOE is studying their use in relation to solvent use.

Voluntary reductions / Codes of Practice

Agreements on reducing the solvent content of paint (largely decorative and architectural) have been reached between industry and government in Denmark, Netherlands and France. These seem an ideal method of reducing VOC emissions in the manufacture and use of coatings. However, without legislative back-up there is a potential problem of equitable enforcement on industry and the achievement of reductions in time scales to meet environmental and political agendas.

Those companies operating to Environmental Management Standards(BS 7750) and to industry environment management codes of practice (CIA Responsible Care Programme) or participating in the EU Environmental Management and Audit scheme (awaiting adoption in member states) have undertaken a commitment to reduce the environmental impact of their operations and products. These companies include the larger multi-national decorative and industrial coating manufacturers. This voluntary action should reflect in reductions in plant VOC emissions and possibly the solvent content of paint. Larger multi-national coating users also operate to such schemes again offering the prospect of reduced plant emissions. However, small and medium size manufacturers and users rarely do.

Public awareness(consumer pressure)

Eco- labelling is one method of influencing customer choice in an environmentally positive way. France, Germany, Netherlands, and the Nordic countries have existing Eco - Labelling schemes each with different VOC content criteria.

A European regulation (Council Regulation EEC 880/92) is in place establishing a voluntary consumer goods Eco-Labelling scheme. Criteria, based on Life Cycle Analysis, have been developed for interior decorative paint. In respect of VOC's the proposed criteria are:

class1: flat (walls/ceilings) <30 g/l : aromatics <0.5 %(w/w) paint.
class2: gloss (trim paints) <250 g/l : aromatics <5% (w/w) paint

where VOC is defined as any organic compound with a boiling point lower than or equal to 250C at normal pressures. Thus the proposals are expected to be adopted and a scheme introduced this year.

EUROPEAN (EU) LEGISLATION
(The exit or a dead end?)

Framework

EU legislation provides an umbrella framework for legislation in member states. The legislation process is primarily based on consensus between the EU institutions and between member states. The Commission, the administrator of EU policy, initiates legislation by way of a proposal. Consultation with industry usually takes place at the drafting stage. A formal published proposal is subject to scrutiny and possible amendment by the Economic and Social Committee and the Parliament before the Council of Ministers adopt it as legislation This which may establish minimum standards (e.g. AQ or emission limits) or harmonise existing national laws to maintain free market (e.g. machinery and safety), emerges in the form of regulations, directives, decisions or resolutions. These are implemented, directly in the case of regulations or with some discretion, through National laws.

The Commission has a mandate through the Treaties of Rome, Paris and Maastricht to introduce measures which:

- ensure a free market by establishing minimum standards and harmonising existing regulations in member states.
- protect human health and the environment
-improve standards of living

Framework Action Programmes define Commission environmental policy (photochemical oxidants were first addressed in the 1973 programme). Specific objectives in relation to VOC emission control are to:

- ensure co-ordinated air quality and emission measurements across member states and to secure information dissemination.
- evaluate risks to human health and the environment
- adopt ambient air quality standards for ozone and particular VOCs
- develop effective control programmes to ensure establishment and maintenance of air quality standards

Air Quality Standards

There are no statutory air quality standards (protection against acute health effects) or guideline values (defence against long term chronic effects) for VOCs. They are being considered for known carcinogens such as benzene and 1,3 butadiene, but these substances are of little direct relevance to coating operations, except so far as they may be trace contaminants in raw materials.

Ambient air ozone guideline values (table.1) have been established throughout the Union as a result of the directive[10] on air pollution by ozone.

Table 1 Ambient Air Ozone Concentration Guide Values

	1 h Mean	8 h mean
EU Ozone Directive		
health protection threshold	-	50 ppb
vegetation threshold	90 ppb	
Public information threshold	85 ppb	
Public warning threshold	20 ppb	
WHO	76 -100 ppb	50 -60 ppb

An air quality standard[11] is in place for NO2 (annual limit value(98% percentile of hourly average): 200 $\mu g\ m^{-3}$) which is to be attained by 1997 . Where areas have ambient levels outside the limit and values can't be met within required time scale, member states are required to establish plans (by 1994) to bring areas into compliance by progressive improvement over shortest period of time. The directive also contains a standstill clause such that there should be no significant deterioration of air quality outside urban areas.

The proposed framework directive[12] on Air Quality Assessment and Management proposes the introduction of regional air quality zones viz.

poor - member states required to produce improvement plans
improving- no increase in pollution allowed
good -no particular requirement.

and paves the way for further air quality standards to be set (ozone in 1996, benzene and PAH in 1999) in the Union. Individual member states are to be charged with meeting air quality standards through National pollution control laws. While laudable in attempting to focus action on problem areas this proposal would work against equitable treatment of industry across the Union and neglects the transboundary nature of the issue.

Pollution Control:

The principles underlying the development of European pollution control measures include:

- prevention at source and minimising risks to human health and the environment through a substance and source directed multi-media approach
- the polluter pays
- resource conservation
- economic feasibility
- economic development (competitiveness)
- international co-operation

There is debate on whether control should be exercised through promulgation of European wide emission standards or that framework controls should establish air quality or emission reduction targets with selection of industries for control and control measures left to individual states. This is a difficult judgement to make, since the first approach leads to commercial equity while the second leads to equitable environmental quality, both fundamental principles in the Union.

There is also debate on whether emission standards should be based on the maximum available control technology irrespective of cost or on best available techniques taking into account cost impacts. The first approach can lead to a requirement to apply a control particular technology while the second allows control flexibility. Clearly, the judgement has to be based on evaluation of the economic (including environmental) and welfare risks associated with particular pollutants.

The EU, recognising the multi-media pollution potential of industrial operations has recently published a proposal[13] for integrated pollution prevention and control. This effectively brings together, and expands to cover land pollution, directive 84/360 EEC on control of air pollution from industrial plants and directive 76/464 EEC on pollution caused by certain dangerous substances discharged into the aquatic environment. The proposed directive will require member states to introduce a national permitting procedure for facilities in the chemicals, energy, mineral, metallurgical, waste and other industries where the potential for pollution is large. Plants producing resins, monomers and other paint raw materials and intermediates will be subject to the procedure if they produce amino, chloro or organo-metallic compounds or their capacity exceeds 1 tonne per day. Coating operations come within the scope of the proposals if their total consumption of organic solvent is greater than 200 kg/h (approximately 1000 tonnes per year). Recent developments include a proposal to reduce this solvent use threshold to 100 kg /h (or 100 t.p.a.). Other coating operations may be covered by daughter directives under this framework.

The permit is to contain conditions for preventing, wherever practicable, or minimising releases to air, water and land. This is likely to require operators to carry out a full environmental impact assessment and to consider plant life cycles. While the proposed directive does not include limits for releases to each of the media, Member States will be required to set these, or equivalent parameters, for a wide range of polluting substances including VOCs. The limits set are to be based on Best Available Techniques and should ensure Environmental Quality Standards are not breached. Where EQSs are being met by less rigorous release controls than achievable using BAT, greater emissions may be allowed. This provision, in conjunction with the proposal to designated air quality zones, may pave the way for tradable permits.

The directive was scheduled to enter into force by 30 June 1995 with new facilities and existing plant in areas where EQSs are being violated being expected to comply immediately and other existing plant by 2005. There has been some slippage in the enactment schedule, but the proposal is expected to take a high priority within the legislative programme. a directive may adopted in the next 12 months.

The coatings industry is concerned that the recently proposed solvent use threshold will subject a substantial number of moderately sized operations to more intensive control than they are currently subjected to, with a consequential increase in pollution control costs. However, the directive is based on sound pollution control principles and addresses the problem of harmonisation of control measures across the Union.

A focus for coating industry attention over the last 5 years or so has been Commission proposals for a directive on the limitation of the emissions of organic compounds resulting from solvent use in industrial processes. The latest proposal,

dated July 1994, is the 7th unpublished draft released for comment. While the aim of reducing VOC emissions and features of the proposal have remained through out its life the scope and detail of the proposal have been subject to considerable debate with the industry and a consequence of the proposal has been the development of concerted European industrial action by paint and solvent producers and users (CEPE, CEFIC, AUGLEME). This debate has resulted in substantial modification of the proposals from the first draft, notably in the areas of solvent use thresholds, obtaining exemptions for control action already taken and for the use of low VOC content coatings. Attempts to accommodate industry's concerns have resulted in a fairly complex draft of the proposal (it includes 23 annexes detailing the specific technical requirements). In total 20 (originally only 6) solvent using processes (responsible for about 34% of total EC emissions) are addressed in the proposal, those related to coating are listed in table 2.

The proposal will apply to both new and existing plant and contains the following features:

- **process registration:** The registration requirement is based on the mass of solvent used by a facility and this varies with process type and production throughput. It is notable that coating manufacture has been included in the plants for control as this is estimated to be responsible for 0.7% of the European solvent emission.
- **solvent management plans:** A solvent mass balance to include releases to effluent and fugitive emissions.
- **integrated pollution control:** The air pollution control objectives should not be met at the expense of discharges to land or water. Recovery and recycling of solvent is to be encouraged and permit conditions are to address energy saving.
- **emission limits**

These are based on health and environmental risks and on BAT.
Organic solvents containing compounds which are classified as Carcinogens, mutagens or toxic to reproduction [R45, R45, R47, R49, R60, R61] are to be replaced with less harmful material with minimum delays and to be reduced to lowest level technically achievable. Emissions limited to 2 mg/m3 where the emission of the sum of these compounds >10 g/h
Chlorinated organic solvents: 20 mg/m3 where total emission of these compounds > 100 g/h
Total hydrocarbon (as carbon): the limits proposed vary with type of process and throughput (table 2).

- **exemptions for the use low organic solvent content products.**
- **compliance deadline deferment:** for installations applying abatement measures before directive comes into force
- **exemption from total hydrocarbon emission limits:** if National Plans produce equivalent total reductions 10 years after adoption of the directive.
- **limitation of fugitive emissions:** The limitations required depend on the process.

-Table 2. Solvent Directive Proposal Processes

Process	Organic Solvent Use t per annum (kg / h)	Emission Limit mg(C) m^{-3}	Fugitive Limit % solvent input
surface cleaning	1(1) R45 and Cl solvents 2(2) other solvents	20 to 50 100	10 to 15 15 to 20
coating processes of new cars	15(15)	Ovens: 50 Total 45 to 120 g/m^2 body area	
coating processes of truck cabins	15(15)	Ovens: 50 Total: 55 to 65 g/m^2 body area	
coating processes of vans and trucks	15(15)	Ovens: 50 Total: 70 to 90 g/m^2 body area	
coating processes of buses	15(15)	Ovens:50 Total: 150 to 210 g/m^2 body area	
vehicle refinishing	None	50 (guide value)	25
coil coating	25(25)	50	5 to 10
coating of metallic and plastic surfaces	5(5) 15(15)	150 50	25 20
coating processes of wooden surfaces	5(5) 15(15)	150 Applic.100 Dry. 50	25 20
coating processes of textile, fabric, film and paper surfaces	5(5) 15(15)	150 Applic 100 Dry. 50	25 20
manufacture of coatings, varnishes, inks and adhesives	100(100)	150	3 (>1000tpa) 5(< 1000tpa)

economic instruments: The proposal permits these put is not specific.

- **emission monitoring:** continuous monitoring if total carbon emission > 10 kg/h: periodic monitoring if total carbon emission > 1 kg/h.

The need for and general aim of the proposed control is accepted by industry, after all every one benefits from clean air even plant managers. The current proposals are regarded as allowing a flexible approach to pollution control and establishing a reasonably level commercial playing field across the Union. Key remaining industry concerns are:

- **Solvent use limitation over emphasised:** This can compromise product quality , productivity, process operability and economic performance with little general environmental benefit[14]. Industry prefers controls on specific organic compounds.
- **a poor perceived balance between costs and environmental benefits.** The total cost of implementing the directive has been estimated to be about $85 billion (about $2 billion per annum for the painting industry) and lead

to a 60% reduction (from 1 million tonnes) in annual solvent emissions. However, this has not been translated into anticipated reductions in ambient ozone concentrations or reductions in adverse health effects.

- **unrealistic limits for carcinogenic and chlorinated material.** Emissions from coatings are not regarded as a significant threat to health or the environment. This criticism may not be valid if longer term chronic effects are taken into account.
- **focus on coating industry solvents:** Undue emphasis when energy, transportation, agriculture and natural sources can, through release of VOC, NOx and CO, make a significant contribution to ambient ozone levels.
- **demands for information excessive:** Resulting in excessive cost.

The scheduled time for introduction of a directive was 1994 with implementation by member states in 1996. This is clearly unlikely and, despite broad agreement on the latest draft, it is understood that the proposals are to revised substantially as a result of a proposed intention to make the "solvent directive" a daughter directive of the IPPC directive. A revised draft proposal is anticipated in the next 3 to 6 months. To eliminate overlap with an IPPC directive, proposals for a new "solvent directive" are likely to primarily address those plants falling within scope of IPPC (i.e. those plants using more than say 100 kg/h or 100 t/a solvent). For these plants the main features of the existing directive would be preserved along with a specific requirements for control of water and land pollution introduced by IPPC. It is understood that general (not operation specific) emission limits will be proposed. Those plants falling below IPPC thresholds are likely to be covered by setting a national emission reduction target, possibly around 50%, which will be specified in the directive, and leaving National authorities to specify the detail of control measures required to meet the target over say10 years. Such a proposal, while possibly, simplifying the directive will set negotiations with industry back. The time scale of the Solvent Directive illustrates the difficulties in obtaining consensus and it is unlikely that a directive will be issued in the next 12 months, possibly delaying implementation in member states till 1997 or after.

Such delays permit evaluation of the effects of existing VOC emission control measures and the introduction of ozone air quality standards at a potential cost of economic disadvantage to those member states where controls are already in place.

CONCLUSIONS: THE FUTURE

(Break out)

There is concern that average ambient air ozone levels are increasing and that there are European regions where World Health Guidelines for ground level ambient ozone concentrations are being exceeded and that this will be remain so even if the current 30% VOC emission reduction target is met. Some are of the opinion that VOC reductions of the order of 70% are required to redress the problem. The prospect is therefore for further demands for VOC and other ozone precursor emission reductions towards the end of the millennium, probably as a result of the 1996 review of the Geneva Protocol.

Industry is responsive to need for controls on VOC emissions and are actively participating in legislation development. Development of EU legislation has resulted in

the emergence of European wide coating industry lobbying groups. To be effective in legislation formulation and in developing industry led alternatives, these groups have a wider role in co-ordinating the collection and dissemination of information.

Primary industry concerns are the level of emission control required and the timing of legislative measures because of the commercial consequences. Clear emission targets, taking into account cost considerations, accompanied with a reasonable implementation period mitigate these concerns. The prospect of further controls on VOC and NOx emissions while still trying to meet existing obligations is discomforting.

Achieving lower ozone levels may mean extending VOC emission controls to smaller operations because in many nations large VOC emitters are already subject to control. Also low cost conservation and process efficiency measures will have been the prime means of achieving a 30 % reduction. Thus further reductions in emissions is likely to incur greater marginal expenditure.

Emission inventories compiled to prioritise the sources for emission control, should not be restricted to particular groups of VOC sources or solvent users. Ozone formation is a complex problem involving several precursors and VOC emissions from sources other than coating operations. Proposals for emission controls on coating operations which neglect these factors are unlikely to encourage support from the industry.

Without ambient air pollution measurement, an understanding of the relationship between pollutant emissions and their ambient air concentrations and air quality standards based on risks to the human health and environment, it is difficult to establish effective and economic emission control programmes at international, national or even facility level. Effective and economic implementation of the principle of source control also relies on understanding the chemical nature, quantities and sources of emissions and their fate in the atmosphere. Thus it is the industry's and in regulator interests to encourage rather than resist emission measurement. If the cost of such measurements is beyond some enterprises the significant national and international interests would seem to suggest a case for employing the economic instrument of a subsidy. Paint manufacturers should consider undertaking their own research in areas.

Increasing understanding of the nature and toxicology of emissions from coating plant in addition to environmental impacts during coating life cycle may lead to rationalisation of VOC emission controls. If this is to be done there is a need take an integrated view of the net environmental impacts of coatings and the coating industry (as is being done in the revisions of environmental law in Denmark) through further life cycle analysis. The rationalisation may take the form of greater emphasis on photochemical reactive and toxic emissions instead of total hydrocarbons, thus leaving some flexibility in coating formulation to achieve desired coating properties.

Regulators and small to medium size coating users favour coating solvent content restrictions and the substitution of solvent based coatings with low or no VOC coatings to reduce emission levels, because it is perceived as a low cost emission

control option. However, the costs associated with the substitution and coating functional performance compromises are often overlooked. Equally, when the life cycle impacts are considered, net environmental benefits may not be achieved. Substitution can not therefore be necessarily regarded as a universal economic option

For Eco-Labelling schemes to be effective the criteria for award should be based on sound and critical life cycle analysis and not on arbitrary targets to reduce solvent use in the products they are applied to.

VOC emission controls applied to coating operations vary widely throughout the Union. Harmonisation of industrial pollution controls will follow EU legislation based on emission standards. Legislation based requiring member states to relate the level of required pollution control to air quality is unlikely to result in commercially equitable controls on industry. However, this is probably the best environmental option. Thus, if environmental protection is the prime aim of the legislation, greater emphasis should be placed on the promulgation of air quality standards which clearly set pollution objectives. Attainment and maintenance of these objectives within a specified period consistent with environmental risk should be the basis of pollution control measures required of companies, leaving the mechanics of doing this to plant operators.

International issues have tended to shift industry attention from local issues such as the odour associated coating operations. The genuine, but in the majority of cases unnecessary, fears of health and environmental risks engendered are bad for the industry image highlighting it as a major polluter and are costly to individual companies. Eco- labelling should not be regarded as a substitute for objective information which raises the public knowledge of the environmental risks and benefits associated with surface coatings. Development and dissemination of such information might well be considered by the industry groupings which have resulted from consideration of European directive proposals.

There is rationalisation in the coating market supply side - international leaders are emerging - and there is internationalisation of manufacturing. Such multi-national companies voluntarily operate to environmental management standards for commercial reasons. Equally access to finance and insurance for all companies is increasingly conditional upon environmental management systems being in place. Additionally, increased public access to company and environmental information act to motivate environmental performance improvement. Therefore, as a result of a consequential company obligation to continually reduce the environmental impacts of their operations, there is a real prospect of VOC emission reductions through innovation. In these circumstances, with a strong faith in market mechanisms by governments and industry, there is a need to examine the effects of these measures in considering the need for further legislation

A compulsory requirement for companies operate to environmental management standards, along with the application of sector reduction targets, may well provide the most commercially flexible and economic method of attainment of emission reductions without the need for the time consuming development of emission regulations to achieve the same ends.

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COATING ALTERNATIVES GUIDE (CAGE)

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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1.0 INTRODUCTION

Many manufactured items are painted or coated in order to protect the substrate, enhance the appearance of the product, or both. Conventional liquid paints and coatings contain a substantial quantity of organic solvent that evaporates during the curing or drying of the coating. Consequently, surface coating operations are a major source of Hazardous Air Pollutant (HAP) and Volatile Organic Compound (VOC) emissions. According to recent estimates, air emissions from industrial surface coating operations in 1992 accounted for nearly 24 percent of all VOC emissions to air from industrial processes (U.S. EPA 1993). This equaled more than 2.6 million tons (2.4 million metric tons) of VOCs.

As coatings users come under increasing pressure from environmental regulatory agencies to reduce their emissions of HAPs and VOCs, coatings suppliers are rapidly developing new lines of low- and no-VOC/HAP coatings. Due to the pace of new product development, coatings users, particularly small businesses, frequently are not aware of new products and of the degree to which these products can reduce their process emissions. Even when businesses are aware of new coatings, they may question whether these products can meet their operational, aesthetic, and performance requirements.

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[1] RTI would like to acknowledge the contributions of David Williams of the North Carolina Office of Waste Reduction, Vic Young of the U.S. EPA's Waste Reduction Resource Center in Raleigh, North Carolina, Jeffrey Danneman of Reichhold Chemicals, Inc., and Ken Monroe of Research Triangle Institute, all of whom provided technical review and suggestions for the development of CAGE.

To assist the end user with sorting through information about lower-emitting coatings, Research Triangle Institute (RTI) is working in cooperation with the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (AEERL) to develop the *C*oating *A*lternatives *G*uid*e* (CAGE). The goal of this work is to develop a computer-based tool that coating users, and those providing technical assistance to them, can use to select technically appropriate, cost-effective, and low-emitting coatings. CAGE is designed to provide information on coating equipment and chemistries in a user-friendly, decision-tree format.

The technical effort is focused initially on developing CAGE to provide information about alternative coatings for metal parts and products painting. CAGE is being developed in three phases:

1) development of a prototype system using a limited set of coating options,
2) testing the prototype logic system with the help of coating users and state and local pollution prevention assistance offices, and
3) expansion of CAGE to include additional coatings and detailed information about coating options.

This paper describes progress in development of the logic framework for the prototype CAGE system.

2.0 THE CAGE CONCEPT

RTI, in collaboration with EPA, is developing CAGE to address the information needs of smaller businesses that use coatings. It is expected that the primary audiences for CAGE will be those at the business responsible for selecting coatings and the staff of technical assistance programs who conduct pollution prevention assessments for small businesses.

The traditional approach to providing information to smaller businesses generally focuses on gathering information on a topic and creating a written document which is then made available through business assistance hotlines, resource centers, and other distribution systems. Unfortunately, written documents generally have limited utility for meeting the information needs of a small business for many reasons. These include:

Difficulties Disseminating the Documents. For the information to be used, it must first get to the intended audience. Many times businesses are not aware of the existence of the document, do not know where to obtain the document, or find that the copies of the document they would like are not available.

Information Is Not Complete. Many times resource guides do not have complete information about all relevant options, so that the information seeker must identify, locate, and read multiple documents in order to have complete information about relevant options.

Documents Include Information Irrelevant to the User. For written documents on

complex subjects, such as coatings, to be of use to a broad audience, they must contain a tremendous amount of information. However, only a small portion of that information is likely to be directly relevant to the needs of a particular user. This forces the user to search through the document to determine which portions may be relevant--a time-consuming process that may deter small businesses from examining the information.

Information Is Not Current. The "shelf life" for a written document in a rapidly changing field such as coatings technology may be as short as a year or less. This time frame may be even shorter if the document contains information such as names and telephone numbers of product vendors or technical contacts. Most guides are not updated or are updated infrequently.

The difficulties in gathering and distributing coatings information suggest an information diffusion approach based on electronic information media. Electronic media provide the ability to manufacture and distribute essentially unlimited copies of information virtually instantaneously and at little cost. Diverse sources of information can be collected into a single information base, to which information can be easily added over time. When information is updated, it can be made available almost immediately. Electronic media also lend themselves to user-directed information searches which allow the user to screen out irrelevant information.

The development of CAGE is based on the premise that an electronic information base available for personal computers can serve as an effective tool to assist coatings users (and the organizations that provide technical assistance to them). These users need not only information about the coating chemistries that can reduce emissions from coating operations, but also expertise to help focus their search on those coating chemistries that can best meet their specific performance and other requirements. To meet these needs, CAGE will provide 1) information about a variety of low-emitting coatings and 2) a relative ranking of coatings based on information provided by the user about a specific application.

The ranking of options is based on the user's answers to a series of questions about performance requirements, operational limitations of the painting line, appearance requirements, and cost considerations. CAGE does not rank coatings based on environmental factors. CAGE includes information only about lower-emitting coatings; conventional low-solids, solvent-borne coatings are not in the system, and, therefore, are not ranked.

The rationale for developing CAGE is similar to that for the *S*olvent *A*lternatives *G*uid*e* (SAGE), which RTI developed in collaboration with the EPA, to identify alternative cleaning chemistries and equipment for small businesses. SAGE has been used successfully to distribute information about alternative cleaning options to a broad audience. More than 2,000 copies of SAGE have been distributed to date through EPA electronic bulletin boards and EPA's Control Technology Center. Many of the users of SAGE are small business assistance providers that take laptop computers to small businesses and run the SAGE program to identify cleaning chemistry and equipment options while they are conducting pollution prevention assessments. New versions of SAGE continue to be developed and distributed through the Internet. It is expected that CAGE will be as successful as SAGE in helping to disseminate information to small

businesses.

Because CAGE is primarily aimed at small businesses, the system is currently being developed using expert system software that runs in a DOS operating system. A DOS-based system was chosen rather than a Windows system because many small businesses that have computers are using older AT-based computers operating with DOS systems and may not have the hardware to adopt Windows.

3.0 TECHNICAL DEVELOPMENT OF CAGE

The remainder of this paper focuses on the development of the logic system in CAGE for ranking coating options. The development of the logic system for ranking options in CAGE consists of three main parts:

1) developing the set of coatings to include in CAGE,
2) developing the set of questions that will be used to elicit key applications information from the user, and
3) developing the logical reasoning and scoring systems that determine how the user's answers to the questions affect the ranking of coatings.

Each of these items is discussed below.

3.1 Coatings Included in CAGE

The alternative coatings included in CAGE represent "generic" formulations rather than specific vendor products. This approach was selected for several reasons. Although including specific coating formulations in CAGE would provide the user with more detailed information about coatings, doing this would require the use of information from coatings vendors about the characteristics of their products. It would not be possible to verify all vendor claims about their products. In addition, including specific product formulations in CAGE would create a situation in which CAGE would be ranking rival products from vendors for particular applications. This would not be appropriate because in many cases vendors formulate products specifically to meet the demands of the customer's application. In addition, a single vendor may offer a large and diverse product line that changes as new products are introduced. Including all of these in CAGE and keeping information in the system current would be expensive and extremely difficult. Finally, CAGE is not intended to be a replacement for the technical representative of the coatings vendor. Rather, CAGE is intended to narrow the range of formulations that the coatings user investigates. CAGE also can help the user understand performance issues and limitations of certain classes of coatings so that the user can be more knowledgeable about coating options when contacting a vendor.

Several generic coating systems are included in the current prototype for CAGE. Each of the coating chemistries in the system is currently available with VOC and HAP contents less than 3.5 lb/gal (420 g/l). Current systems are divided into primers and topcoats. The types of coatings included in these categories are shown in Table 1.

Table 1. Coating Selections Available in CAGE

Primers	Topcoats
Alkyd (high solids, solvent-borne)	Alkyd (high solids, solvent-borne)
Alkyd (water-reducible)	Alkyd (water-reducible)
Epoxy (2-component, solvent-borne)	Latex
Epoxy (2-component, water-reducible)	Powder (baked finish only)
Latex	Acrylic
	Epoxy
	Polyester
	Urethane (2-component)
	Urethane (1-component, baked finish only)

The expected VOC content range for these formulations will depend on whether the coating is an air dry, baked, or 2-component coating. Typical VOC content ranges for these coatings are shown in Table 2.

Table 2. Approximate VOC Content Range for Coating Selections

Coating Type	Approximate VOC Content Range	
	lb/gal	g/l
2-Component	2.8	335
Latex	1.5	180
Powder	~ 0	~ 0
Solvent-borne air dry	2.5 - 3.5	300 - 420
Solvent-borne baked finish	2.0 - 2.8	240 - 335
Water-reducible air dry	2.5 - 3.0	300 - 360
Water-reducible baked finish	1.5 - 2.5	180 - 300

The initial set of coatings included in CAGE has been limited intentionally to simplify the development of the prototype system. This set of coatings was selected to provide a representative sample of alternative system chemistries currently available, and will be expanded as the logic for the system is refined and verified.

3.2 Information Gathered by CAGE to Rank Alternative Coatings

Developing a ranking of potential coating alternatives requires a variety of information from the coating user regarding the operational, performance, appearance, and other requirements of the coating system. The system gathers information by asking a series of questions similar to those a coatings "expert" might ask of a user in order to narrow the list of likely coating selections.

CAGE begins by requesting information about the user's current process in order to determine whether the user is seeking to choose a primer, a topcoat, or both. The program then gathers information about the current coatings that are being used, the types of cleaning and pretreatment that are conducted, the application equipment that is currently used, the number of color changes that typically occur during a day, and the current curing method (air dry, force dry, or baked). This information helps to establish a "baseline" for the type of coating needed.

Coating selection is also based on the substrate material. CAGE is currently being developed to address metal parts coating, with a focus initially on steel and aluminum substrates which are the major metallic substrates used in manufacturing. Future development of CAGE may include other metal substrates as well as non-metallic substrates such as wood and plastics.

The system then gathers information about the relative importance to the user of coating appearance, compared to the performance characteristics of the coating. Coating selection in certain cases is primarily a matter of selecting a coating that looks good (e.g., the metal components of a stapler); whereas, in other cases, the coating must be able to protect the substrate from corrosive environments (e.g., metal components of outboard motors). In some cases, both properties are important (e.g., certain automotive components). The user's selection will determine whether high performance coatings will be weighted more strongly.

CAGE then asks questions regarding the types of operational and performance requirements that the user has. Operational requirements indicate how quickly the coating must dry or become tack-free in order to ensure that the current rate of production is not compromised. Performance requirements relate to the level of physical and chemical stress that the final dry coating must be able to withstand, such as sun exposure, heat, chemical resistance, abrasion resistance, and impact resistance.

Finally, the system considers a user's willingness to change current equipment, and the degree to which cost considerations will affect the selection. Users who are unwilling to modify their current application equipment or who are unable or unwilling to spend more for their coating will be more constrained in their choice of alternatives than users who may be willing to consider redesign of their current coating line or a more expensive coating option in order to reduce their emissions.

3.3 Solution Ranking by CAGE

Information regarding the logic of selecting coatings was gathered primarily through a series of interviews with coating experts. This information was supplemented with additional information from the literature regarding coatings properties.

In general, alternatives in CAGE are ranked based on the user's response to questions. "Scores" for each option are tallied by the system based on the user's response to each question where scoring occurs. For the prototype, alternatives receive a higher score if the coating will do a good job of meeting the user's need, a lower score if the coating does not meet the user's need effectively, and no change in score otherwise. If a coating cannot be used for the user's current

operation (e.g., if the finish is baked and the user does not have, and will not purchase, the necessary curing equipment), the coating is eliminated from further consideration.

CAGE keeps track of each coating's score, based on the user's response to questions, and also maintains a tally of the maximum score possible for a coating. After all questions have been asked, coatings are ranked based on a score normalized to a top total score of 100 points.

4.0 NEXT STEPS

4.1 Current Plans

CAGE is still in the early stages of development, and much work remains before the system can realize its full potential. Several items that will be addressed as this research continues are listed below.

Reports. Development to date on CAGE has focused on the logical process for selecting coatings based on user-defined needs. However, an equally important aspect of the system will be the information it provides to the user about the coatings alternatives, their strengths, their weaknesses, and the specific areas that may be of concern given the user's needs and the limitations of the coating of interest. The report will provide the user with the information the user needs to begin discussions with coatings formulators about specific alternative coatings.

Expanded Expert Input. Rankings from CAGE do not represent "right" and "wrong" answers to the question of coating selection, but rather present a relative preference for certain coatings in particular applications, based on the expert experience that has been built into the system. To a certain degree, coating experts may disagree as to the "best" coating selection for a given application, especially when ranking the "generic" options which are included in CAGE. As CAGE development continues, additional experts will be consulted regarding the logical selection process. This will help ensure that the results from CAGE will not be biased by the preferences of a single coatings expert.

User Testing. The questions used in CAGE will need to be reviewed and refined to streamline the logical flow and to ensure that the broad range of potential users can understand the questions that the system asks. RTI expects to test the CAGE system through reviews by members of small business technical assistance organizations such as the state and local pollution prevention technical assistance programs that make up the National Pollution Prevention Roundtable. The system will also be given to coatings users to test and identify problems.

Additional Coating Alternatives. CAGE currently contains a limited set of possible coating chemistries. RTI will gather further information about coating systems and add them to CAGE to provide a broader set of possible alternatives for the user to consider.

Providing "Transparent" Logic. While obtaining a ranking of possible alternative coatings may be useful to the user, of equal interest may be the logical reasoning behind why

CAGE ranked coatings a particular way for a particular scenario. If CAGE operates as a "black box," the user will not have access to valuable information regarding coating selection. RTI will explore ways to ensure that the logical reasoning in CAGE is "transparent" to the user by providing explanatory notes in the reports provided by CAGE.

4.2 Future Work

Long term development of the CAGE system will seek to expand system capabilities in a number of areas, as described below.

System Maintenance. New developments in coating technology will require that CAGE be maintained and updated in order to stay current.

Coating Equipment Selection. CAGE may be developed to look at not only coating selection, but also coating equipment selection. Coating equipment selection is important not only because it determines the types of coatings that can be used in specific applications, but also because low-efficiency equipment can greatly increase VOC emissions. A more comprehensive CAGE program would consider not only coating selection, but also coating equipment selection.

Additional Substrate Materials. The current focus of CAGE is on aluminum and steel finishing, which is a major sector of the painting market. Other metal substrates could also be added to CAGE. In addition, wood and plastic substrates represent a major portion of paint applications. Future CAGE "modules" could be created to address factors unique to selection of coatings for these substrates.

Windows-based CAGE. Since computer operating systems continue to move towards Windows-type operating environments, CAGE could be made available in a Windows-compatible version. This would offer opportunities to add capabilities to CAGE such as graphics and a mouse-driven user interface.

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SESSION 3

RADIATION-CURABLE COATINGS

PAPERS PRESENTED:

"Barriers to the Use of UV and EB Technologies"
by
Jill Vitas
TRC Environmental Corporation
Chapel Hill, North Carolina

"Environment and Technology Teamed for Economic Sustainability"
(Paper not available for publication.)
by
Al Paskonis
NIST Great Lakes Manufacturing Technology Center
Tucson, Arizona

Arcylate Lesquerella Oil in Ultraviolet Cured Coatings
by
Thomas Schuman
University of Southern Mississippi
Hattiesburg, Mississippi

Volatile Contents of UV Cationically Curable Epoxide Coatings
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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Barriers to the Use of UV and EB Technologies

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ABSTRACT

Surface coating is the process by which paints, inks, varnishes, adhesives, or other decorative or functional coatings are applied to a substrate (e.g., paper, metal, plastic, wood) for decoration and/or protection. This can be accomplished by brushing, rolling, spraying, dipping, flowcoating, electrocoating, or specialized combinations/variations of these methods. The substrate and the coating formulation are two important factors that influence the selection of a coating application process. Once the coating is applied, it is cured or dried using thermal energy or radiation energy in the form of ultraviolet (UV) and electron beam (EB). This paper briefly discusses technical, economic, and educational barriers to radiation-curable coatings in each of the three industries studied.

BACKGROUND AND PURPOSE

In support of the Pollution Prevention Act, the Source Reduction Review Project (SRRP), and Maximum Achievable Control Technology (MACT) standards development, EPA's Air Pollution Prevention and Control Division (APPCD) is investigating pollution prevention opportunities for product and material substitutions that help industry to reduce waste.[1,2]

Radiation-curable coatings have been demonstrated to reduce pollution in several specific end-use categories.[3,4,5] There are two types of radiation curing processes currently in use: ultraviolet (UV) curing and electron beam (EB) curing. UV-curing equipment consists of a UV lamp suspended above the coated substrate, a light reflector, a radiation shield, and a cooling system. The UV-curable coating contains a photoinitiator which initiates the polymerization of the coating to the substrate when exposed to UV light. In the EB-curing mechanism, an electron beam excites the electrons in the coating and causes them to crosslink without the aid of photoinitiators.

ADHESIVE-COATED AND LAMINATED SUBSTRATE MANUFACTURING

This industry is the largest source of methyl ethyl ketone and third largest source of toluene emissions.[6]

Technical Barriers[3]

Raw material availability and the sensitivity of the curing process to the characteristics of the coating and the substrate are major barriers. UV energy does not penetrate thick, dark, or colored coatings well, leaving much of the coating uncured. EB electrons cure 100% of solid adhesives, allowing it to be used on a variety of substrates. Many substrates are sensitive to heat and chemical elements making it necessary to modify conventional UV lamps. Since heat is not a concern in EB-curing, it can be successfully used with heat-sensitive substrates.

Economic Barriers[3]

Capital Costs: Information provided by a supplier of EB-curing and thermal machinery indicates that solvent-based systems (not including emissions control equipment) have higher investment costs. For retrofit, a facility would need to add the EB-curing mechanism; however, a German manufacturer stated that UV-curing mechanisms are more affordable than EB systems.

Operating Costs: Raw material costs are the primary operating cost for any adhesive coating manufacturer. On an applied-solid basis, the cost of UV adhesives is approximately the same as the cost of conventional rubber-based adhesives. The cost of EB adhesives, however, is about 33% more. In the case of conventional acrylic-based adhesives, UV and EB adhesives cost 50% and 88% more, respectively. EB-curable adhesives are best suited for products which require thick coating weights, where they outperform the other conventional and UV-curing technologies.

Educational Barriers[3]

The cost of newly installed radiation-curing equipment should approximate that of new thermal-curing machinery without control equipment. The productivity of the radiation-curing equipment exceeds that of the thermal system, resulting in lower costs and higher profits. Employees must be trained to properly handle these coatings. Although non-hazardous, radiation-curable coatings can cause allergic responses.

METAL CAN MANUFACTURING

This industry emitted over 16,000 tons (14,500 tonnes) of air pollutants in 1992.[6]

Technical Barriers[4]

Product Performance: The product performance problems of ink pick off, poor abrasion resistance, yellowing overvarnish, and off-shade whites were experienced. The UV-curable coatings used by Coors Brewing Co. achieve a level of abrasion resistance high enough to meet the standards of other can manufacturers.

Another barrier is the lack of an FDA (Food and Drug Administration)-approved UV-curable coating for direct contact with food, including beverages. Ball Corporation claimed that components of the exterior UV-curable coatings migrated to the interior of the cans after the cans exited the UV-curing oven. However, Coors conducted 3 months of analyses using Fourier Transform Infrared technology and gas chromatography/infrared detection instruments and found no volatile components from exterior inks or coatings on the internal coating of its cans. Tests have shown a loss of coating weight in the internal coating ovens, indicating that waterbased external coatings also may have a migration problem.

Health and Safety: Through recent advances in monomer chemistry, hazards associated with radiation-curable coatings have decreased significantly. There are concerns with human skin becoming sensitized when in direct contact with radiation-curable coatings, and workers are required to wear appropriate personal protective equipment.

Economic Barriers[4]

Capital Investment: The most common deterrent, when initially considering a UV-curing system, is capital cost. However, when adding additional capacity, a plant may consider a UV-curing oven because the thermal system is a larger capital investment. The can manufacturing business operates on low margins and high volume. Therefore, line speed is a critical element to be considered when evaluating new technologies.

Material and Operating Costs: For Coors Brewing Co., the energy savings from its UV-curing oven compensated for the higher price of UV-curable materials. However, due to increased material consumption and, therefore, increased costs, the UV-curing alternative was not economically feasible for Ball Corporation. Another cost barrier is the availability of materials because ink suppliers consider UV-curable products to be a "specialty" line with a limited market. Coors believes that, if other can manufacturers used these products, material costs would fall.

Educational Barriers[4]

One of the most pressing barriers involves the perception of the word "radiation." Although UV-curing ovens harness radiant energy used to cure the coatings, many people are still hesitant about using such equipment. Another perceived problem is worker sensitization to acrylate compounds in the inks and coatings. A previous difficulty that has since been overcome involves oxygen inhibition. Molecular oxygen would react with free radicals in the coating, forming a peroxide. The reactions would deplete the number of free radicals available for polymerization during the curing process, leading to incomplete curing. Coors suppliers have resolved the oxygen inhibition problem through improved coating formulations.

Many industry personnel believe that UV systems are not cost effective; however, the capital expense for a UV-curing oven is no more than for a new thermal line. Studies indicate that UV curing oven maintenance and energy costs are less than those for thermal systems. Increase of raw materials costs may be offset by savings in emissions fees due to fewer releases of volatile organic compounds and hazardous air pollutants.

COMMERCIAL PRINTING

Commercial printing accounted for over 1,300 tons (1,180 tonnes) of total air releases in1992.[6] This paper focuses on wide-web flexographic printing and screen printing

Flexographic Printing

Flexographic printing is the leading printing process in the packaging industry and is gaining ground in other segments of the printing industry, including newspaper and book printing. The focus of this section is on wide-web flexography, typically defined as flexographic printing on substrates that are 36 in. (91 cm) wide or wider.

Technical Barriers

Equipment Suitability. The industry is unsure of the best method to approach conversion: should the UV-curing equipment be retrofit to the existing press, or should a new press be purchased that incorporates the UV system? To date, American companies have concentrated on retrofit solutions, while European companies have focused on designing complete press systems.

Materials Availability. UV-curable flexographic inks have only recently been commercially produced. One major concern is meeting the FDA criteria for direct contact with food. Manufacturers are working with FDA to develop UV-curable inks that meet FDA criteria.

Product and Ink Performance. Print quality, the most important property in printing, is determined by several parameters, such as color density, adhesion to substrate, and dot gain. Except in glossy printing, UV-curable inks perform as well as or better than solvent-based inks.

Health and Safety. Recent advances in monomer chemistry have significantly reduced the hazards associated with UV-curable flexographic inks. The monomers have a high molecular weight which reduces volatility and removes almost any danger associated with vapor inhalation.

There are concerns with human skin becoming sensitized when in direct contact with UV-curable flexographic inks. Also, the potential exists for the ink to be slightly undercured leaving a residual odor as well as residual unreacted monomers on the printed product. Together, industry and the EPA are working to develop an acceptable maximum residual monomer level.

Economic Barriers

The primary economic barriers to switching to UV-cured flexographic printing are the capital cost of new equipment and ink costs. Most UV-curable inks are comparable in price to solvent-based inks on a cost per unit area covered basis. However, white UV-curable inks are more expensive than any other UV-curable inks, while white solvent-based inks are the cheapest.

Educational Barriers

The Print Manager at a German firm using UV-curable flexography noted that about 3 to 4 weeks of on-the-job training is required to train a standard solvent-based press operator to operate a UV-cured press.

Screen Printing

The best known application is printing designs on textiles; however, screen printing is also used on numerous non-textile substrates; e.g., point-of-purchase advertising material, fleet graphics, specialty decorations, and fine art.

Use of UV-curable inks offers substantial economic, process, and environmental benefits including: (1) reduction in required floor space -- large hot-air dryers and drying racks are unnecessary ; (2) increased throughput -- drying is essentially instantaneous; (3) reduction in health and safety hazards for workers exposed to screen printing inks; and (4) reduced cost per unit area printed (UV-curable screen printing inks are applied in thinner layers).

Technical Barriers[5]

Because of curing difficulties, it is necessary to use inks which achieve the proper opacity with a thin layer of ink. Substrates with deeply textured surfaces may present barriers to screen printing with UV-curable inks. Ink in the deep recesses of surfaces not exposed to sufficient light may not cure properly, resulting in poor adhesion of the ink layer to the substrate. UV-curable inks do not stand up well to finishing procedures after printing, such as die-cutting and molding. Another barrier is the lack of FDA-approved UV-curable inks for packaging that contacts food.

Many signs and labels must withstand extended outdoor exposure or harsh industrial environments. One of the largest markets of this type is fleet graphics, or the large signs that are placed on the sides of tractor-trailer trucks. UV-curable inks are not capable of meeting the expected standard of a 6- to 7-year ink life.

Economic Barriers[5]

Many U.S. screen printers are medium- to small-sized shops, employing less than 50 people and can not afford the capital investment required to convert to UV-curable inks. A shop

with only one or two production lines would lose a significant percentage of its production capacity during conversion. Benefits of larger printers may not be realized in printing small runs on semi-automatic presses.

Educational Barriers[5]

Although the Screen Printing Association International provides information on UV-curable materials, the availability of the information to small shops may be limited.

CONCLUSIONS

Many barriers must be overcome before radiation-curable coatings can penetrate the industry categories discussed. Many of the barriers are similar across the categories so that the improvements may be transferred from one industry category to another. EPA is developing the Adhesives Alternatives Guide (AAGE), which will provide facilities with a computerized system to assist in the evaluation of alternative adhesives. Working through the Design for the Environment Program, EPA is investigating alternative inks for flexographic printing

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ENVIRONMENT AND TECHNOLOGY TEAMED FOR ECONOMIC SUSTAINABILITY

by

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ABSTRACT

Purpose: Emphasis of waste minimization methodologies merged with advanced technologies to improve both the environment and the bottom line.

Proactive activities in pollution prevention require commitment and vision much like the commitment to develop and implement new and emerging technology. This is a case of the linking of both environmental focus and advanced technology to produce not only an environmentally sound practice but an economically advantageous one.

A waste reduction assessment was conducted at a medium-sized producer of specialized screen printing products. The company occupies about 40,000 ft^2 (3,700 m^2) and employs 200 people. The self-adhesive products are used for identification, decorative trim, and screen printed circuitry for electronic products. With programs in place to produce products with little or no solvent content and efforts to reduce production wastes, the company actively began to implement opportunities identified in the assessment. The aggressive engagement to implement these opportunities has provided realized savings large enough to improve profits by $188,000 per year. These opportunities were found in changes in cleaning procedures for silk screens, the deployment of ultraviolet curable inks, and the development and use of waterbased adhesives and inks.

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ACRYLATED LESQUERELLA OIL IN ULTRAVIOLET CURED COATINGS

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INTRODUCTION

Environmental concerns focusing on the emission of volatile organic compounds (VOCs) can be ameliorated via the development and use of very low- to no-VOC coatings. Ultraviolet (UV) radiation curing is an effective means of incorporating low molecular weight reactive species into high performance, non-volatile polymers. The advantages of UV curing include rapid polymer network formation on heat sensitive substrates, reduced energy consumption, low emissions, and minimal space requirements.[1] When cost is a consideration, UV curing offers additional advantages by eliminating the need for high volume air movement, expensive to operate ventilation systems, solvent recovery units, or air scrubbers. However, more often than not, UV curing is accompanied by appreciable volume shrinkage which can cause loss of adhesion, poor edge coverage, and other film defects.[2]

Lesquerella oil (LO) is a vegetable oil of significant commercial potential and, we believe, can be a valuable raw material for the design and formulation of UV cured coatings. Lesquerella oil is obtained from a promising new oilseed crop, *Lesquerella fendleri*. This domestic renewable resource offers a reduction in America's dependence on imported oils of similar structural features. For instance, LO contains 55-60% 14-hydroxy-*cis*-11-eicosenoic or lesquerolic acid, a 20-carbon fatty acid homolog of castor oil's ricinoleic acid.[3] The hydroxy functional fatty acid offers a reactive site for derivative synthesis such as acrylated LO (ALO). Acrylated lesquerella oil's synthesis, characterization, formulation into, and evaluation of UV cured coatings, are the focus of this work.

EXPERIMENTAL

Materials

Lesquerella oil was purchased from International Flora Technology, Ltd. Methacryloyl chloride (MAC), 2-hydroxyethyl methacrylate (HEMA), sodium hydride (95%), toluene diisocyanate (80% 2,4-TDI and 20% 2,6-TDI), triethylamine, tetrahydrofuran (THF), hydroquinone, dibutyltin dilaurate, sodium hydride, and dichloromethane were purchased from Aldrich Chemical Company. All chemicals were used as received except THF, and it was refluxed over sodium hydride for 1 h and freshly distilled before use.

Oligomeric reactive diluent photomers 3016, 4061, 4094, 4149, 4770, and 6008 were supplied by Henkel Chemical Company. Byk 065 and Byk 325 were supplied by BYK Chemie. Silwet 7604 was obtained from Union Carbide, Irgacure 651 from Ciba-Geigy, and Benzophenone from Aldrich Chemical Company.

Synthesis of Methacrylated Lesquerella Oil

A solution of 50 g (0.092 eq hydroxyl) of LO and 9 g triethylamine in 100 mL of dichloromethane was added to a three-neck, 250 mL round bottom flask, equipped with nitrogen inlet, magnetic stir bar, thermometer, and addition funnel. The flask was purged with a slow flow of nitrogen while the contents were stirred at 30°C. Methacryloyl chloride was added dropwise (10.4 g, 0.1 eq) to the reaction flask over 1 h. After addition was complete, the reaction was continued for 2 h while maintaining a temperature of 25°C with an ice bath. A 4-4.5 μm glass frit Buchner funnel was dried at 110°C for 3 h, cooled to room temperature, and used for salt removal by filtration. The solvents were rotary evaporated *in vacuo*.

Synthesis of Acrylated Lesquerella Oil from Hydroxyethyl Methacrylate

A solution of 16.9 g (0.097 moles) TDI and 0.05 g hydroquinone in 50 mL THF was added to a three-neck, 250 mL round bottom flask equipped with magnetic stir bar, heating mantle, thermometer, condenser, addition funnel, and nitrogen purge through a vacuum adaptor. The stirred flask contents were heated to reflux (70°C). 2-hydroxyethyl methacrylate (12 g, 0.092 eq) dissolved in 100 mL THF was added into the addition funnel and transferred into the flask dropwise over 1 h. The stirred flask contents were maintained at 50°C for 0.5 h. A solution of 0.1 g dibutyltin dilaurate in 10 mL THF was added in one portion to the flask and maintained at 50°C for an additional 0.5 h. Lesquerella oil (50 g, 0.092 eq) was added to the addition funnel and transferred dropwise into the reaction mixture over 2 h. The contents were then maintained at 50°C for 1 h. Finally, 0.65 g (0.005 eq) HEMA was introduced in one portion to the reaction

mixture to end cap any remaining isocyanate. THF was removed from the final product by rotary evaporation *in vacuo*.

Characterization Methods

A Bruker AC-200 (200 MHz, $^{1}H/^{13}C$ dual probe) spectrometer and a Nicolet IR/42 FTIR spectrophotometer were used for nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopic analysis, respectively. Nuclear magnetic resonance samples were dissolved in deutero-chloroform spiked with tetramethylsilane for reference. Fourier transform infrared samples were analyzed as a film smear on polished NaCl.

Coating Formulations

The raw materials used in the filler and finish coatings are contained in Table I.

A 100% solids wood sealer formulation containing pigment, additives, photoinitiators, ALO, and acrylic monomers and oligomers, was dispersed for 0.5 h to a Hegman 7 grind using a 3.5 in cowles high speed mixer at 1500 rpm. The UV wood filler formulations are included in Table II. The sealer was applied on sanded poplar with a draw bar at 2 mils wet thickness, and subsequently cured via UV radiation for 7 sec at 11 cm from a 300 W medium pressure mercury UV lamp.

The 100% solids wood and metal finish coatings were formulated with the materials of Table III and prepared in a manner identical to the filler coatings. The finish coatings were applied at 2 mils wet film thickness with a draw bar onto a lightly sanded sealer coating (wood), chromate treated aluminum (American Society of Testing and Materials Method (ASTM) D-1750, Type B, Method 2), or cold rolled steel panels. The applied finishes were irradiated under a 300 W medium pressure mercury UV lamp for 7 sec at 11 cm distance.

Coating Characterizations

Pencil hardness and cross-hatch adhesion tests were performed according to ASTM D-3362 and ASTM D-3359, respectively. Impact resistance was measured with a BYK-Gardner heavy duty impact tester, Model IG-1120 with 1.8 kg (4 lb) mass and 1.59 cm (0.5 in) diameter round peen. Yellowness indexes were measured by the Applied Color System CS-5 Chroma-Sensor. Specular gloss was taken with a Gardco Statistical Novogloss as specified by ASTM D-523. Dry film thicknesses were determined by a Gardco Minitest 4000 Microprocessor coating thickness gauge. Chemical resistance was analyzed through a 2 h spot exposure test according to ASTM D-1308. The tensile strength and percent elongation were determined by an MTS Model 810. Thermal analysis was performed with a Mettler TA4000 system equipped with a DSC 30 measuring cell under a nitrogen purge (25 cc/min) and at a heating rate of 10°C/min.

Table I. Raw Material Descriptions

Materials	Molecular Weight	Acrylate Functionality	Function
HEMALO	1996	1.6	Monomer
MACLO	1084	1.8	Monomer
Photomer 3016	452	2	Monomer
Photomer 4061	300	2	Monomer
Photomer 4094	428	3	Monomer
Photomer 4149	428	3	Monomer
Photomer 4770	--	--	Oligomer
Photomer 6008	--	--	Oligomer
Byk 065			Defoamer
Disperbyk 163			Dispersant
OmeyaCarb F			Pigment
Byk 325			Mar-slip
Irgacure 651			Photoinitiator
Benzophenone			Photoinitiator
Silwet 7604			Surfactant

Table II. Ultraviolet Cured Wood Filler Formulation

Materials	Amount (g)
Photomer 4061	26
Photomer 4094	20.5
Photomer 4149	12
Photomer 4770	5
Photomer 6010	5
Disperbyk 163	1
OmeyaCarb F	30
Benzophenone	1.5
Irgacure 651	1

Polymer Swelling Experiments

The extent of crosslinking was determined from swelling experiments of free films. Films were obtained by draw downs onto polyethylene, and subsequent curing with UV as described. Free films were removed from polyethylene and fashioned to approximately 2 X 0.1 mm dimensions, placed on a microscope slide, covered with a flat glass cover slip, and viewed microscopically at 18X magnification. The microscope was equipped with an ocular scale for millimeter measurements. After the film dimensions were measured, several drops of methylene chloride were placed at the slide/cover interface. Swelling occurred immediately and was complete in less than 1 min after which 5 individual measurements of the swollen film were taken and used for determination of the swelling ratio (see Table IV). The swelling ratio was calculated as the ratio of the length of the swollen film (L_s) to that of the initial and unswollen (L_o) film.

Table III. Ultraviolet Cured Lesquerella Oil Acrylate High Gloss Wood Finish Formulation

Materials	1 Amount (g)	2 Amount (g)	3 Amount (g)
HEMALO	--	15.1	--
MACLO	--	--	15.0
Photomer 3016	16.1	16.4	16.0
Photomer 4061	20.0	20.1	20.1
Photomer 4094	17.0	17.2	17.1
Photomer 4149	4.1	4.3	4.2
Photomer 4770	5.0	5.1	5.0
Photomer 6008	10.0	10.2	10.2
Byk 065	0.4	0.4	0.4
Byk 325	0.5	0.5	0.5
Irgacure 651	2.1	2.5	2.5
Benzophenone	1.1	1.3	1.3
Silwet 7604	0.3	0.4	0.3

RESULTS AND DISCUSSION

Synthesis

Lesquerella oil methacrylate was synthesized by the reaction of MAC with LO (Scheme 1). Structural characterization was performed via FTIR and ^{13}C-NMR spectroscopy.

The FTIR spectrum of LO (Figure 1) offers characteristic hydroxyl (-OH) absorption centered at 3454 cm^{-1} and carbon-carbon double bond (-C=C-) absorption at 1598 cm^{-1}. Ester formation gives rise to a new absorption in the 1598 cm^{-1} region accompanied by the disappearance of the 3454 cm^{-1} hydroxyl absorption.

Table IV. Mechanical Properties and Solvent and Chemical Resistance of Lesquerella Oil Acrylate Coatings

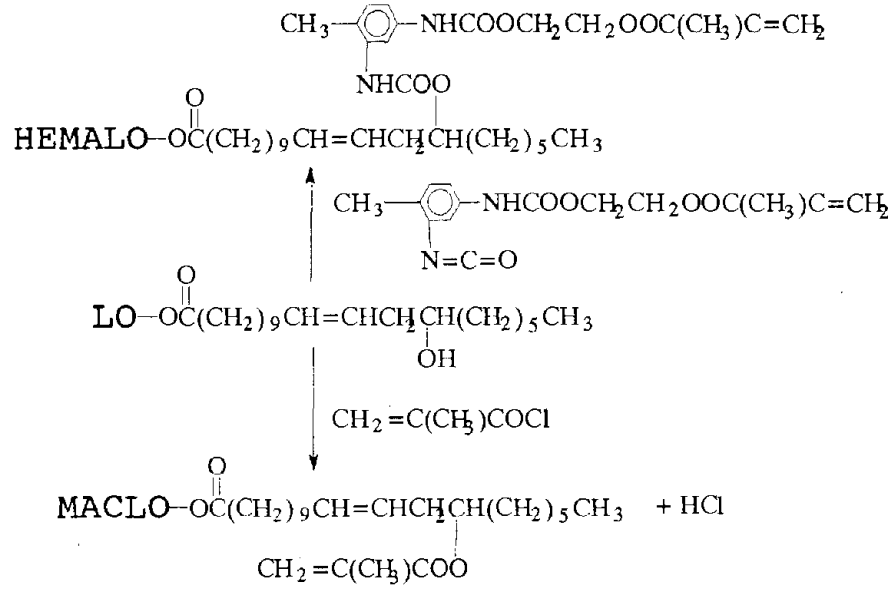
Formulation #	1	2	3
Tensile Strength (psi)	2928	2220	1894
Percent Elongation (%)	5.5	6.1	5.4
T_g (°C)	45	51.4	42.3
Linear Swelling Ratio	1.111	1.108	1.150
MW per X-link	115	106	138
MEK Double Rubs (on steel panel)	350 (2 mil)	310 (2 mil)	220 (2 mil)
2 h Spot Test (ASTM D-1308)			
20% H_2SO4	5	5	4
Soap Solution	5	5	5
D.I. Water	5	5	5
Vinegar	4	4	4

Additional structural confirmation was obtained from ^{13}C-NMR analysis (Figure 2). The C_{14} hydroxyl bearing carbon of LO absorbs at 71.453 ppm, while the adjacent C_{13} and C_{15} carbons absorb at 35.32 ppm and 36.81 ppm, respectively.[4] Ester formation shifts the absorption of the oxygen bearing carbon

downfield to 74.0 ppm, while the C_{13} and C_{15} absorptions move upfield to 31.50 and 33.33 ppm, respectively.[5]

Coatings prepared exclusively with MACLO were soft, and adhered poorly to metal surfaces. In an effort to improve film properties, aromaticity was introduced via reacting TDI with HEMA and LO to give HEMALO according to Scheme 1.

TDI was initially combined with HEMA in a 1:1 molar ratio to produce the acrylic-isocyanate intermediate, which was subsequently reacted with LO to give the desired product, HEMALO. The synthesis of HEMALO was confirmed by FTIR (Figure 1) and ^{13}C-NMR (Figure 2) analyses. The FTIR spectrum of HEMALO experienced a shift of the free hydroxyl absorption from 3454 cm^{-1} to 3341 cm^{-1} with derivative formation, and the 1600 cm^{-1} absorption



Scheme 1: Synthesis of MACLO and HEMALO from LO

broadened and intensified signaling the presence of the acrylate double bond and benzene's aromaticity. The ^{13}C-NMR spectrum of HEMALO showed decreased absorptions at 71.45, 36.81 and 35.32 ppm, and the appearance of absorption frequencies at 76.00, 33.69, and 31.66 ppm, signaling acrylic ester formation.

The amount of acrylic functionality added to LO was calculated from ^{1}H-NMR spectral integration (Figure 3). The fraction of the acrylic moiety compared to fatty acid was determined via the ratio of the absorption area corresponding to

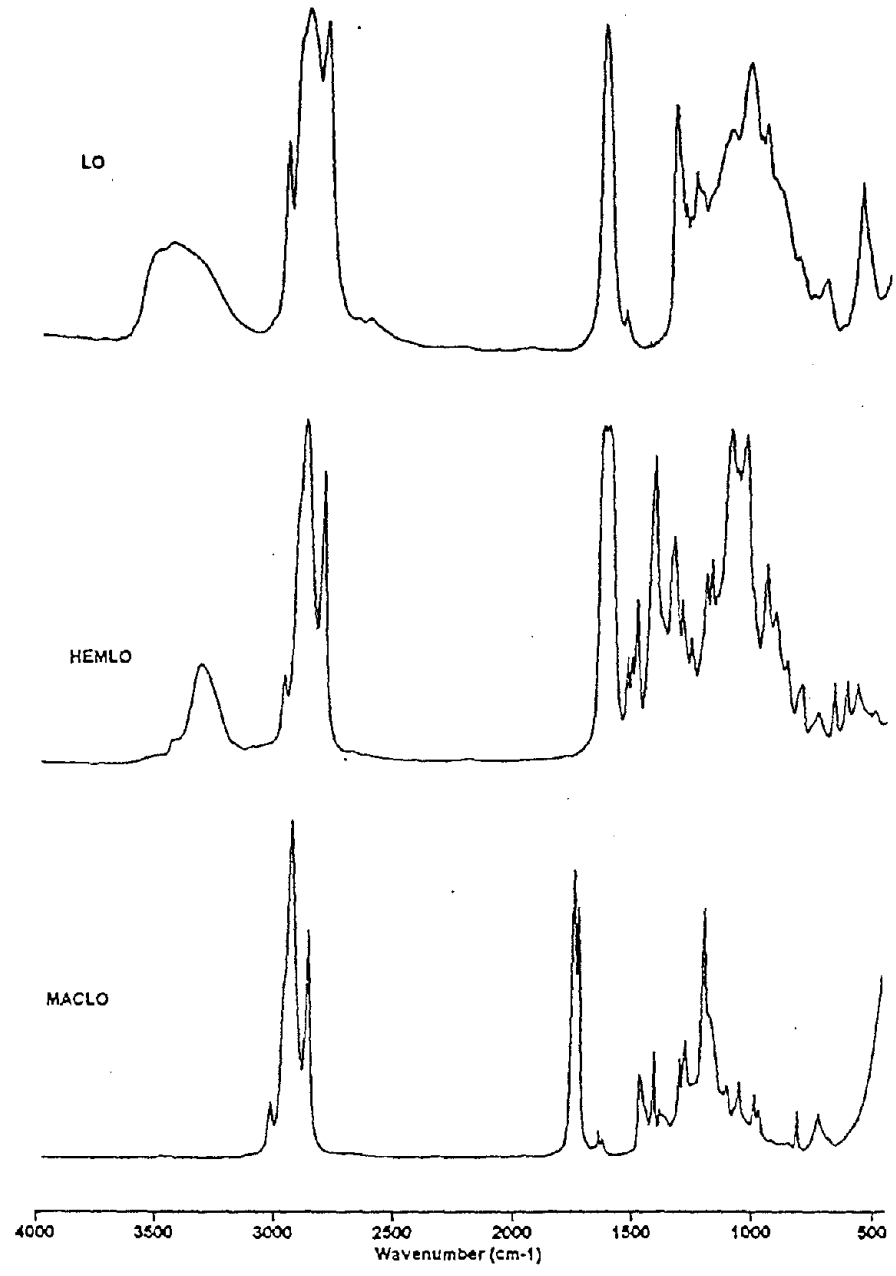


Figure 1: FTIR Spectra of LO, HEMALO, and MACLO

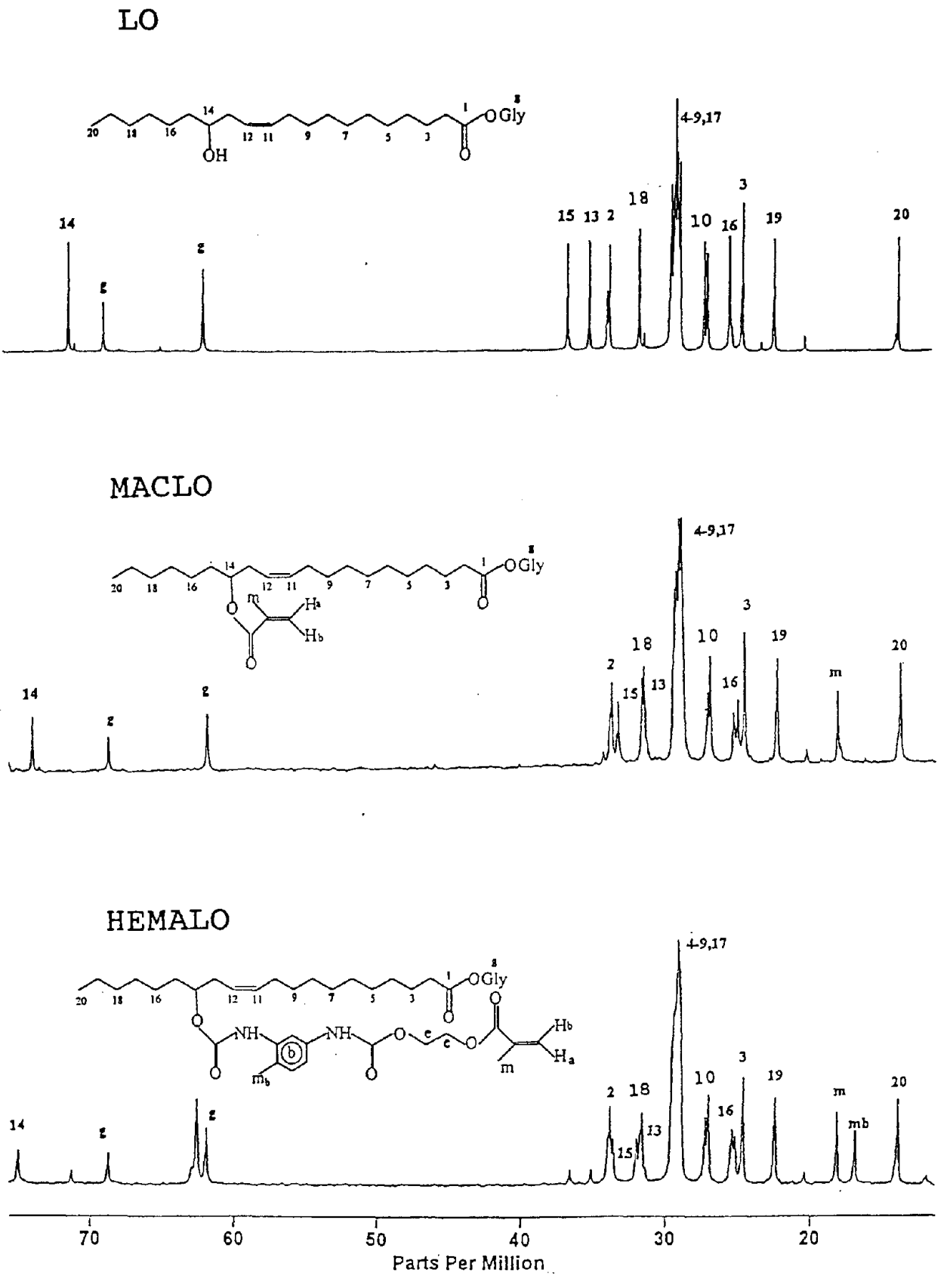


Figure 2: Carbon-13 NMR Spectra of LO, MACLO, and HEMALO

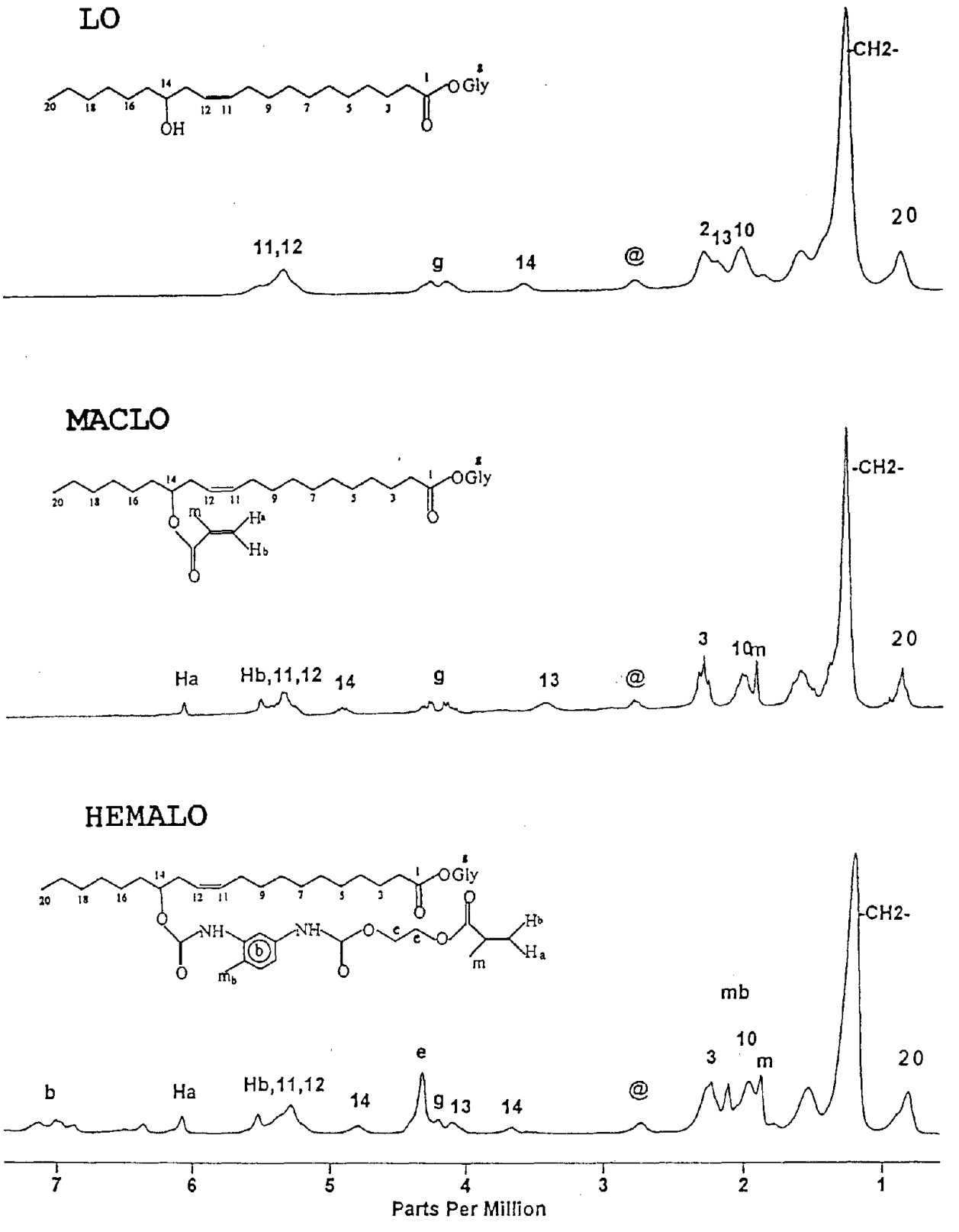


Figure 3: Proton NMR Spectra of LO, MACLO, and HEMALO

the trans alkene proton (AHa) to the area corresponding to the C_{20} methyl protons (A20) according to Equation 1:

$$r = \frac{\int AHa}{\int A20} \qquad [1]$$

The calculated values of acrylation are enumerated in Table V. Based on ^{1}H-NMR spectrum of LO, the mole fraction of hydroxy fatty acids of LO is 0.55,[6] and if one makes the assumption that no side reactions occur, the theoretical acrylic/fatty acid ratio is equal to the hydroxy fatty acid fraction, 0.55. In practice, MACLO derivation was determined to be 0.54, or a 98% theoretical conversion. For HEMALO, additional HEMA was added to end-cap unreacted TDI after reaction of the HEMA/TDI intermediate with LO. Therefore, the acrylate/fatty acid ratio was larger than theoretical although there remained some unreacted hydroxyls in HEMALO.

Table V. Fraction of Acrylate Group Relative to Fatty Acid

Derivative	Theoretical Acrylate/Fatty Acid Ratio	^{1}H-NMR Calculated Acrylate/Fatty Acid Ratio
MACLO	0.55	0.54
HEMALO	0.55	0.61

Swelling Experiments

Swelling of the UV cured films was performed with methylene chloride. The Flory-Rehner equation (Equation 2) was employed to calculate the molecular weight between cross-links and the cross-link density of the films:[8,9]

$$-[\ln(1-\upsilon_2) + \upsilon_2 + \chi_1(\upsilon_2)^2 = V_1 n[(\upsilon_2)^{1/3} - \upsilon_2/2] \qquad (Equation\ 2)$$

where ν_2 is the volume fraction of polymer in the swollen mass, χ_1 is the Flory-Huggins polymer-solvent dimensionless interaction term, V_1 is the molar volume of the swelling solvent, and n is the number of active chain segments per unit volume. The number of active chain segments per unit volume (n) equals ρ/M_c, where ρ is the polymer density and M_c is the molecular weight between crosslinks. The published interaction parameter in chlorinated solvents indicates a value in the range of 0.4-0.5,[10] while our efforts determined an interaction parameter of 0.5. The molar volume of methylene chloride is 64.2 mL/mol. The swelling ratio and the calculated M_c experimental values are given in Table IV.

Swelling data provides overall crosslink density and polymer segment molecular weight between crosslinks. Coating #3 was the least crosslinked (138 g/crosslink) followed by coatings #1 (115 g/crosslink) and #2 (106 g/crosslink). This is not unexpected as Coating #3 contained the modified oil and thus two crosslinks per LO molecule are possible (approx. MW = 982 g/mol), or a theoretical 540 g/crosslink based solely on MACLO. Since excess hydroxyethylmethacrylate was added, TDI-diethoxymethacrylate was likely formed to some extent and thus reduced the weight per crosslink.

Coating Physical Properties

Coating properties are shown in Tables IV and VI. All coatings showed excellent gloss (~80 @ 20°), adhesion (5B), and pencil hardness on wood panels. When a wood filler was used as a first down coating, pencil hardness and adhesion was improved. The gouge pencil hardnesses for coatings #1 and #2 (9H) outperformed coating #3 (6H). Moreover, coating #3 (MACLO) gave the lowest tensile strength and glass transition temperature (T_g), which we have attributed to insufficient cure[7]. This was confirmed via swelling ratios (see Table IV) which demonstrated that coating #3 had the highest and coating #2 the lowest swelling ratio, respectively.

Coatings formulated with ALO were superior to the control with respect to direct and reverse impact resistance on cold rolled steel. Cross-hatch adhesion confirmed poorer adhesion to steel for the control (1B, or 20%) than either coating #2 (4B, 80%) or #3 (5B, 100%). Moreover, coating #2 possessed better cross-hatch adhesion to aluminum (3B, 60%) than either coating #1 or #3 (0B, 0%).

The UV cured coatings demonstrated excellent chemical resistance (Table VI), where MEK resistance followed the order of Coating #1 > coatings #2 > coating #3. A 20% H_2SO_4 solution treatment did not change the appearance of coatings #1 and #2, but stained coating #3, a likely result of lower crosslinking density.

CONCLUSIONS

Acrylated lesquerella oil derivatives were synthesized for the first time, and formulated into UV cured coatings. Structural characterization was performed by FTIR, ^{1}H-NMR and ^{13}C-NMR analyses. The use of MACLO in UV curing coating formulations provided for improvements in flexibility[11] and adhesion to metal. Coatings formulated with HEMALO showed significantly improved adhesion to both steel and aluminum substrates. Lesquerella oil modification increases flexibility at the expense of T_g and solvent resistance.

Table VI. Physical Properties of Lesquerella Oil Acrylate Coatings

Formulation #	1			2			3		
	Wood	Al	Steel	Wood	Al	Steel	Wood	Al	Steel
Specular Gloss 20°	85	95	93	81	100	72	76	84	79
(ASTM D-523) 85°	99	100	98	98	100	96	97	96	98
Yellowness Index		1.3			2.3			3.0	
Gouge Hardness by Pencil (ASTM D-3363)	9H	F	8H	9H	4H	7H	6H	5H	7H
Direct Impact (ASTM D-2794), (lb-in) (J)			40 (4.5)			80 (9.1)			70 (7.9)
Reverse Impact (ASTM D-2794), (lb-in) (J)			5 (0.6)			20 (2.3)			20 (2.3)
Cross-Hatch Adhesion (ASTM D-3359)	5B	0B	1B	5B	3B	4B	5B	0B	5B

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VOLATILE CONTENTS OF UV CATIONICALLY CURABLE EPOXY COATINGS

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INTRODUCTION

Ultraviolet cationically curable epoxide coatings are used for protecting metal and inks in rigid packaging applications and as overprint varnishes for plastic tubes. Excellent adhesion to metal and plastic and toughness during post-forming are benefits of cationic epoxide chemistry and requirements of these applications. The cycloaliphatic epoxy resins used in these coatings are low viscosity and low odor. Coatings can be formulated with low application viscosities without adding solvent; therefore, the coatings have very low volatile organic contents. This paper reports findings from measurements of the volatile contents of starting-point formulations using ASTM D 5403-93 and identification of volatiles by analytical techniques.

EXPERIMENTAL DETAILS

Coating volatile contents were measured in triplicate following ASTM D 5403-93 Test Method A, including Note 3 for UV cationic epoxide coatings. Coating weights ranged 0.2- to 0.4-g and the substrate was 4- X 12-in. aluminum panels for volatile content measurements. Coatings samples for the FT-IR/TGA, GC/MS and water titration experiments were obtained by curing the coatings on glass plates and scraping coating samples off the glass. The coated aluminum panels and coated glass plates were cured using 250 mJ/cm^2 UV dose supplied by a LINDE® UV cure unit operated with a 400 W/in. mercury-vapor arc lamp and the conveyor at 90 fpm.

FT-IR/TGA is a hyphenated technique that simultaneously records the thermogravimetric (TG) weight loss and the FT-IR spectra of effluent gases without operator intervention.[1] The FT-IR/TGA instrument was from Bio-Rad, Cambridge, MA and consisted of a Bio-Rad FTS60 FT-IR spectrometer and an Omnitherm TG analyzer. The Bio-Rad minicomputer, in addition to performing its normal FT-IR functions, controlled the operation of the TGA. This enabled the TG and FT-IR data to be coordinated in time in one computer, and for the spectral data to be correlated with the observed weight losses. A temperature program was set up which raised the temperature from 20 to 110 °C at 10 °C/min, held it there for 35 min before continuing at 20 °C/min to 800 °C for 7 min. The ramp to 800 °C was to prepare the equipment for the next sample.

The samples were analyzed using Headspace Gas Chromatography. The instruments were an AutoSystem gas chromatograph interfaced with HS-40 Headspace Sampler, both from Perkin Elmer. The samples were heated in 22-mL headspace vials in the sampler at 110 °C for 1-h. A DB-1 (30- X 0.53-mm i.d., 5-μm film) megabore column was used with a split of 5/1 and a column flow of 8 mL/min helium. The oven program was 60 °C for 4 min, ramp at 10 °C/min to 260 °C. The injection port temperature was 200 °C and the flame ionization detector temperature was 260 °C. The HS-40 needle and transfer temperatures were 130 °C, and the pressurization time and injection time was 0.2 min. Gas chromatography/mass spectrometry

(GC/MS) was conducted using an HP-5890 gas chromatograph interfaced with an HP-5970 mass Selective Detector, both from Hewlett Packard.

A Mitsubishi Moisture Meter Model CA-05 and Water Vaporizer Model VA-05 were used to analyze coating volatiles for moisture. Approximately 0.3-g samples were introduced into the boat and purified and dried nitrogen was passed over the samples with a flow rate of 200 mL/min for 1-h. The VA-05 was maintained at 110 °C during this time. The water was determined by coulometric titration. The reagents were Mitsubishi Aquamicron AU and Aquamicron CK. Replicates were tested. All the water was evolved from the coating samples within the first 30 min.

Two DEFENSOR 3100 humidifiers were used to maintain constant high relative humidity (RH) when UV curing coatings for volatile content and surface-cure rate measurements requiring constant high humidity. Sealed chambers containing desiccant or a saturated $ZnSO_4$ solution were used to store coated panels during the 48-h equilibration for volatile content measurements conducted with the equilibration close to 0% and at 90% RH, respectively.

Surface-cure rates were measured by lightly touching coating surfaces with a cotton ball immediately after UV curing. The conveyor speeds, measured in feet per minute (fpm), at which no cotton fibers adhered to coating surfaces were recorded as the surface-cure rates. Coatings were applied to aluminum foil-coated paper and cured using a 400 W/in. mercury-vapor arc lamp for surface-cure rate measurements.

The cycloaliphatic epoxide resins 3,4-epoxy cyclohexylmethyl-3,4-epoxy cyclohexyl carboxylate (EEC) and bis(3,4-epoxy cyclohexylmethyl) adipate (BEA), polyester diol (hydroxyl no. 212) and triol (hydroxyl no. 560), epoxidized linseed oil (LOE), and mixed triaryl sulfonium hexafluorophosphate salts 50 wt% solution in propylene carbonate (PI solution), were obtained from Union Carbide Corporation. Dipropylene glycol diglycidyl ether (DPGDGE) was obtained from The Dow Chemical Company. Castor oil was obtained from CasChem, Inc. Indicating DRIERITE® (anhydrous calcium carbonate) was obtained from W. A. Hammond Drierite Company and $ZnSO_4 \cdot 7H_20$ from Mallinckrodt. All materials were used as received.

RESULTS AND DISCUSSION

ASTM 5403-93 Method B Note 3 specifies that cationic epoxide coatings which gain weight while heating 1-h at 110 °C should equilibrate for 48-h at room temperature after UV curing and before heating. The coatings presented in Tables I-IV gained weight as a result of UV curing and two gained weight as a result of heating (coatings **G** and **H** in Table II).

The weight gain has been attributed to atmospheric moisture reacting with cationic coatings.[2] The superacid (HPF_6), which is generated from photolysis of the cationic photoinitiator ($Ar_3S^+PF_6^- \rightarrow HPF_6$), is hygroscopic and its appearance greatly increases coating hygroscopicity.

The FT-IR/TGA method was used to identify the major volatiles from coatings **A** and **C**, the ingredients of which are provided in Table I. Within the first 15 min of each FT-IR/TGA experiment, an evolved gas was detected whose weight fraction varied between 1 and 3% of the total weight. Volatile loss was complete within 35 min of heating at 110 °C during the TGA experiments. Figure 3 shows a representative profile of the evolved gas. The FT-IR spectra of sample **A** and **C** were similar; Figure 4 shows a typical spectrum. The main bands are observed at 1858 cm^{-1}, due to carbonyl stretch, and near 1107 cm^{-1}, due to ester type C-O stretching band. The FT-IR spectrum corresponds to propylene carbonate (PC) gas, the PI solvent.

GC/MS identified PC as the major volatile and identified traces of phenyl sulfide, the PI photolysis product. Phenyl sulfide was not detected in the FT-IR spectra probably because its concentration was too low to be detected. FT-IR/TGA and GC/MS experiments conducted on coatings **A** and **C** found no evidence of epoxy resin or polyol in the volatiles. The titration method confirmed the presence of water in the volatiles.

In some cases in the results in Tables I and II the amount of potential volatiles was significantly less (**E-H**), approximately the same (**A**, **C** and **D**) and significantly more (**B**) than the amount of PI solution in the formulations. High coating T_gs and high boiling points of volatiles would be expected to slow diffusion of volatiles from coatings while heating. Not all of the PC and phenyl sulfide may evaporate while heating because their boiling points are high (240 and 296 °C, respectively). Water absorbed during UV curing and equilibration which reversibly hydrated the coating would most likely be evaporated completely while heating because the boiling point of water (100 °C) is less than the bake temperature (110 °C) and water absorbed during UV curing and equilibration would reside mostly at the coating surface. Coating T_g dramatically increases during UV curing and high T_g would limit diffusion of absorbed water into the lower coating layers. Water at the surface could be volatilized without complications from diffusion effects. The relative amounts of PC and water in the volatile mix of a cationic epoxide coating may depend on factors such as the amount of PI solution the coating contains, coating T_g, hygroscopicity of coating ingredients and the RH during UV curing. The volatiles in excess of the weight of PI solution in coating **B** were most likely water. Coating T_gs probably limited the amount of volatiles by limiting diffusion in cases (**E-H**) where volatile contents were less than the weight of PI solution.

The process weight gains and potential volatiles of coatings **A-E** (Table I) were significantly larger than those of coatings **F-H** (Table II). The differences between results in Tables I and II were perhaps due to differences in the amount of PI solution the coatings contained, differences in the hygroscopicity of ingredients, differences in RH at the time of the measurements or some combination of these explanations. The RH was not measured when the results in Tables I and II were obtained.

Comparing the results among Tables I and II suggests volatile contents depend on the amount of polyol a coating contains. The amount of water absorbed during UV curing was inversely proportional to polyol concentration in Tables I and II. Coatings **A** and **E** contained polyester diol and castor oil, respectively, and coatings **B-D** contained no polyol. Coatings **A** and **E** gained about half the weight coatings **B-D** gained during UV curing. The same trend was demonstrated by the process weight gains of coatings **F-H** but the weight gain differences among these coatings were arguably within experimental error. The potential volatiles of coatings **F-H** were proportional to polyol concentration. The potential volatile differences among coatings **F-H** were significant. PC evaporated (the coatings contained 6% PI solution) and water was absorbed as a result of heating and the amount of water absorbed increased with decreasing polyol concentration.

The volatiles of coatings **I**, which contained 19.2% polyol, and **J**, which contained no polyol, were measured using controlled humidity conditions to better understand the effects of RH and the presence of polyol on volatile content results. Coatings **I** and **J** had similar process weight gains and potential volatiles using low humidity UV cure and equilibration conditions (Table III), despite the amount of polyol the coatings contained.

Coatings **I** and **J** had significantly more process weight gain and significantly more potential volatiles when high humidity UV cure and equilibration were used compared to when low humidity conditions were used. The amount of water absorbed during UV cure and equilibration strongly depended on RH. The amount of potential organic volatiles was probably not affected

by the humidity during UV cure and equilibration; therefore, the extra potential volatiles measured under high humidity conditions compared to low humidity conditions was water vapor. Coating **J**, which contained no polyol, gained significantly more weight than **I** during UV curing and **J** lost less weight than **I** during heating using high humidity conditions.

Two mechanisms, which could occur simultaneously, best explain these finding. One mechanism is that polyol hydroxyls and water compete for epoxides in the presence of superacid catalyst. According to this mechanism, the rate of the reaction of epoxides with water was higher in **J** than in **I** because polyol hydroxyls were not available in **J** to compete with water for epoxide. The epoxides acted like a (irreversible) sponge for hydroxyls from water or polyol or both (Figure 1). The other mechanism is that polyol hydroxyls associate with cations, such as superacid (HPF_6) and polymerizing cationic centers, and reduce cation hygroscopicity. Cations act like a (reversible) sponge for hydroxyls and the presence of polyol hydroxyls decreases the rate of hydration of cations (Figure 2).

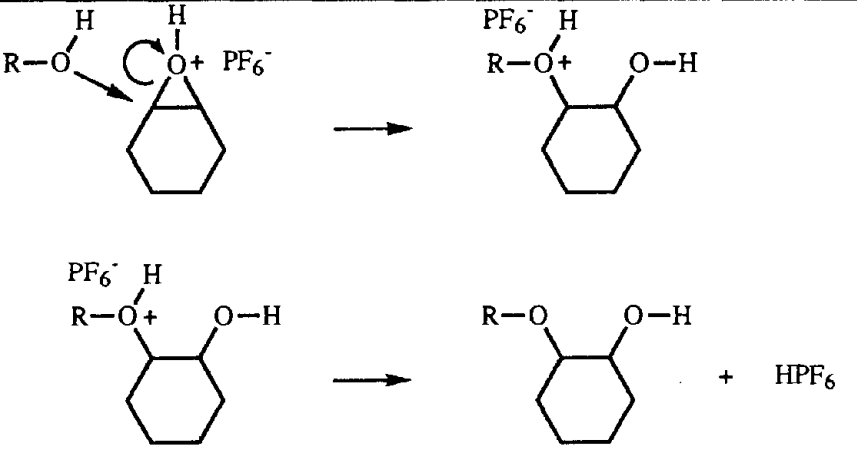

Figure 1. Ring-opening Polymerization Initiated By Hydroxyl, Where R• = H•, $R'CH_2$• (From Polyol), or R"—O

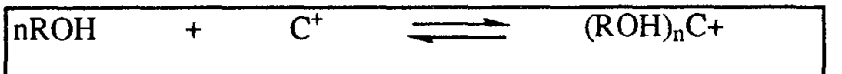

Figure 2. Reaction Of Hydroxyls With Cationic Centers (C^+), Where R• = H• Or Alkyl Radical

Surface-cure rate studies were conducted to better understand the effects of RH and polyol concentration. The formulations in Table IV were used for the surface-cure rate study. A plot of surface-cure rate vs. RH is presented in Figure 5. The surface-cure rates passed through maxima and the positions of the maxima moved to higher RH with decreasing polyol concentration. Atmospheric moisture enhanced surface-cure rates at low RH as demonstrated by the increased cure rates with increasing RH up to the maxima for each polyol concentration. This suggests water absorbed by the coatings acted as initiator for epoxide polymerization. Higher surface-cure rates of coatings containing higher polyol concentrations at low RH suggest that polyol

hydroxyl also acted as initiator for epoxide polymerization. Previous reports described polyols as chain transfer agents for epoxide polymerization.[3] Hydroxyls from water and polyols could play both roles, initiators and chain transfer agents. As initiators, water and polyol would increase cure rates. As chain transfer agent, polyol could increase the rate of gellation or become part of a dangling end. Water could enhance cure rate as an initiator but would produce dangling ends in the role of chain transfer agent.

At RH values above the maxima in Figure 5 the surface-cure rates decreased probably because the rate of ring-opening competed effectively with epoxide polymerization. Ring-opening can lead to dangling ends especially if water participates in the ring-opening reaction (Figure 1). Cationic epoxide coatings with useful physical properties are generally formulated with at least a two-fold excess of epoxides relative to polyol equivalents. Excess epoxide is required to develop high enough crosslink density and T_g via epoxide polymerization to proved useful physical properties.

The viscosities reported in Tables I and III demonstrate that UV cationic coatings containing cycloaliphatic epoxides can be formulated to low viscosities required by some application techniques. The coatings formulations presented also had low odor which is of benefit for plant environments.

CONCLUSIONS

Cationic epoxide coatings were formulated with low viscosities and were found to have very low volatile contents. The major organic volatile was identified as propylene carbonate, the photoinitiator solvent, by FT-IR/TGA and GC/MS and traces of phenyl sulfide, the photoinitiator photolysis product, were identified by GC/MS. Water was identified in the volatiles by titration.

The measurement of volatile contents of cationic epoxide coatings was complicated by the effect of relative humidity. Cationic epoxide coatings absorb atmospheric moisture during UV curing. Coatings containing less polyol were found to absorb more moisture. Cationic epoxide coating absorbed more moisture when the volatile content measurements were conducted at higher relative humidity. Two reactions, reaction with epoxides and hydration of cations, which could occur simultaneously, were proposed to explain the reactions of atmospheric moisture with cationic epoxide coatings.

The reaction of water and epoxide was supported by cases where coatings containing no (or less) polyol absorbed more water as a result of UV curing and had less potential volatiles than coatings containing (more) polyol, and by surface-cure rate studies. Increasing RH increased surface-cure rates up to the maxima.

The reversible hydration of cations was supported by the identification of water by titration as part of the potential volatiles, by findings that the amount of volatiles depended on humidity, and by cases where the potential volatiles were greater than the amount of PI solution in the coating.

References

(1) Compton, D. A. C.; Markelov, M.; Mittleman, M. L.; Grasselli, J. G.; *Appl. Spectrosc.* **1985**, *39*, 909.
(2) Strand, R. C.; Ludwigsen, R. J. *SME Technical Paper FC75-328* **1975**, Society of Manufacturing Engineers.
(3) Crivello, J. V.; Conlon, D. R.; Webb, K. K. *J. Radiation Curing* **1986**, *13*(4), 3.

Table I. Volatile Contents Of UV Epoxide Coatings With And Without Polyol

Ingredients	A	B	C	D	E
EEC	62.4	67.2	67.2	67.2	67.2
Polyester Diol	19.2				
DPGDGE	14.4	28.8			
BEA			28.8		
LOE				28.8	
Castor Oil					28.8
PI solution	3.8	3.8	3.8	3.8	3.8
Surfactant	0.2	0.2	0.2	0.2	0.2
Viscosity 25 °C (cP)	275	200	580	590	455
VOC (ave wt%)					
Process	-3.070	-5.655	-7.476	-6.051	-3.268
Potential	3.860	5.378	3.961	3.344	2.856
Total	0.7898	-0.2768	-3.514	-2.706	-0.4117
Standard Deviation					
Process	0.2612	0.2232	0.2475	0.1585	0.1207
Potential	0.07911	0.2927	0.1286	0.04040	0.1387
Total	0.3120	0.4660	0.3438	0.1229	0.1422

Table II. Volatile Contents Of UV Epoxide Coatings Demonstrating Weight Gain As A Result Of UV Curing And Heating

Ingredients	F	G	H
EEC	68.9	79.3	83.6
Polyester Triol	24.6	14.2	9.9
PI solution	6.0	6.0	6.0
Surfactant	0.5	0.5	0.5
VOC (ave wt%)			
Process	-0.3422	-0.3691	-0.4797
Potential	2.397	-0.9135	-1.259
Total	2.054	-1.283	-1.738
Standard Deviation			
Process	0.07712	0.07526	0.08405
Potential	0.02261	0.1487	0.1471
Total	0.08992	0.1364	0.1871

Table III. Volatile Contents Of UV Epoxide Coatings Measured Using Controlled Relative Humidity

Ingredients	**I**	**J**
EEC	62.4	81.6
Polyester Diol	19.2	0
DPGDGE	14.4	14.4
PI solution	3.8	3.8
Silicone Surfactant	0.2	0.2
Viscosity 25 °C (cP)	275	305
UV Cure Conditions	28% RH	
48-h Equilibration Conditions	Desiccated	
VOC (ave wt%)		
Process	-1.719	-1.992
Potential	3.084	4.286
Total	1.365	2.294
Standard Deviation		
Process	0.5238	0.3860
Potential	0.9376	0.5642
Total	1.186	0.9128
UV Cure Conditions	60% RH	
48-h Equilibration Conditions	90% RH	
VOC (ave wt%)		
Process	-5.797	-9.432
Potential	6.150	5.732
Total	0.3536	-3.700
Standard Deviation		
Process	0.5242	0.1836
Potential	0.4710	0.5563
Total	0.1257	0.4488

Table IV. UV Epoxide Coatings Used For Surface-Cure Rate Measurements

Ingredients	K	L	M	N
EEC	100	95	90	80
Polyester triol	0	5	10	20
PI Solution	4	4	4	4
Surfactant	0.5	0.5	0.5	0.5

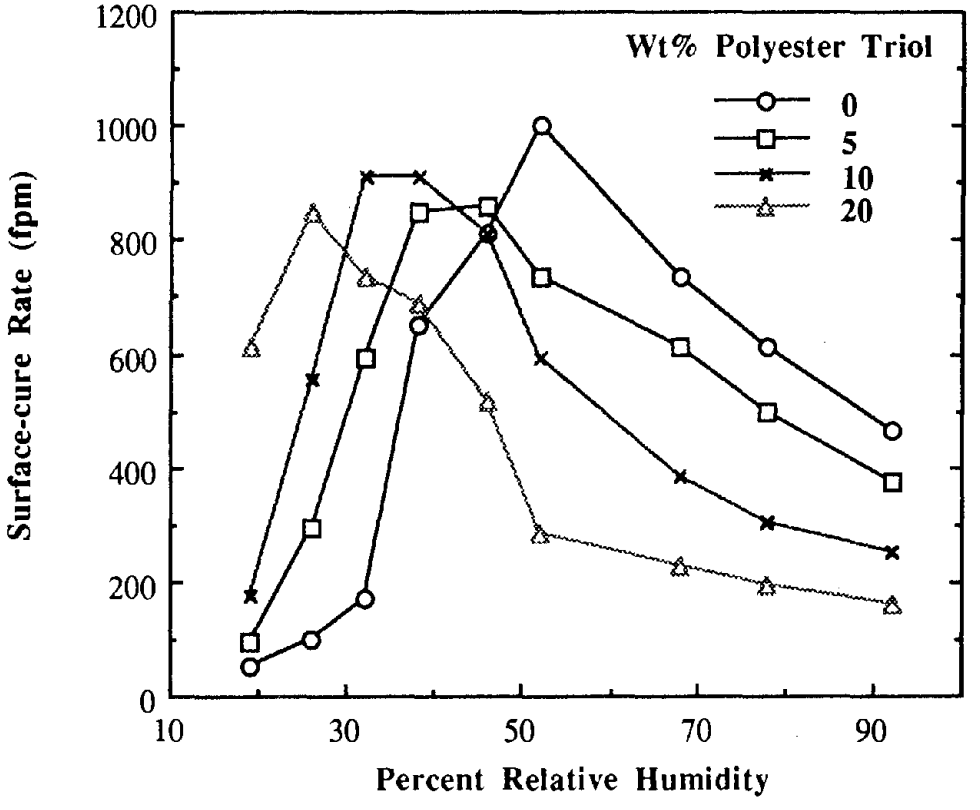

Figure 5. Effects Of Relative Humidity And Polyol Concentration On Surface-cure Rate Of UV Epoxide Coatings

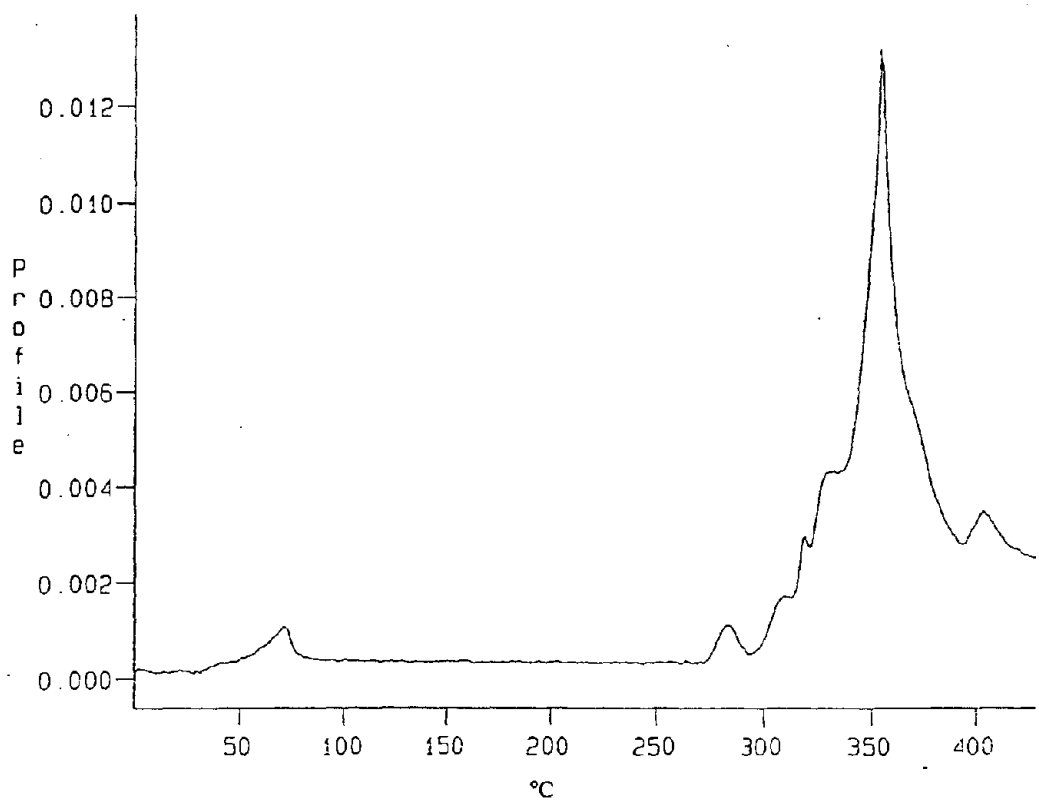

Figure 3. Evolved Gas Profile From FT-IR/TGA Experiment

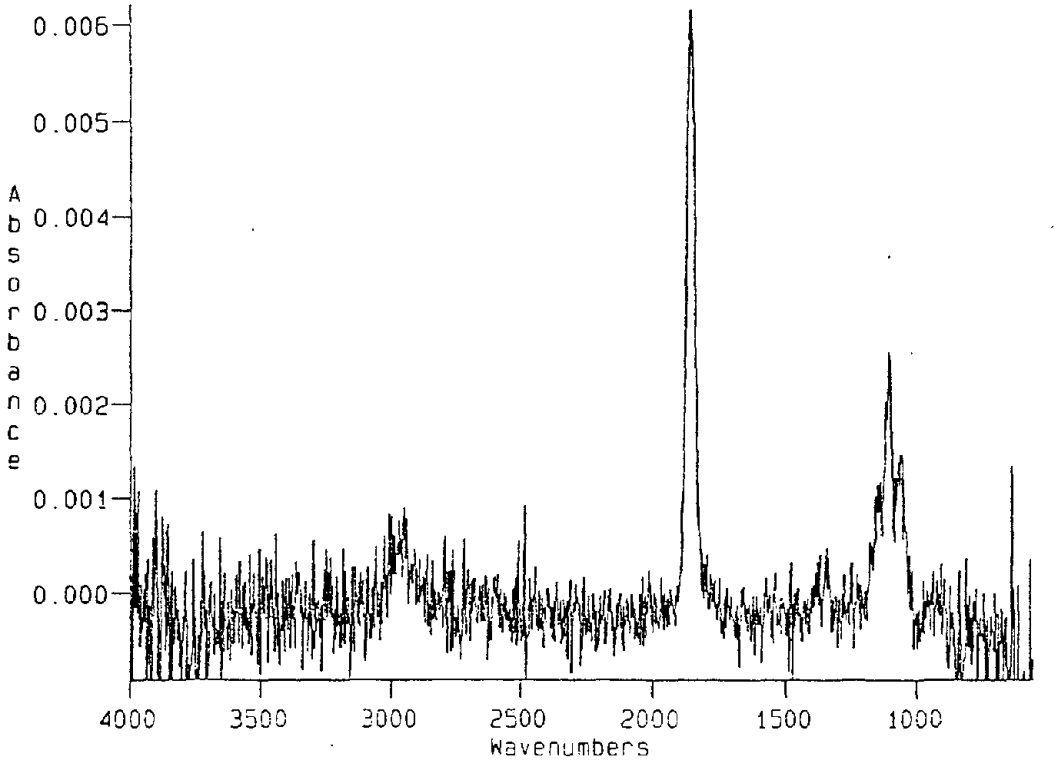

Figure 4. IR Spectrum From FT-IR/TGA Experiment

SESSION 4

LIFE CYCLE ANALYSIS

PAPERS PRESENTED:

"The Use of Life Cycle Assessment in an Ecolabeling Scheme:
The European Ecolabel on Paints and Varnishes"
by
James Besnainou
Ecobalance, Inc.
Rockville, Maryland

"Optimizing Coating Formulations for Total Environmental and Product Performance"
by
Jimmy Bassett
Eastman Chemical Company
Kingsport, Tennessee
and
Don Sullivan
Shell Chemical Company
Houston, Texas

"Life Cycle Analysis of an Aqueous Low VOC Coating"
by
Jack Kowal
Coors Brewing Company
Golden, Colorado

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

THE USE OF LIFE CYCLE ASSESSMENT IN AN ECOLABELING SCHEME:

THE EUROPEAN ECOLABEL ON PAINTS AND VARNISHES

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ABSTRACT

This article demonstrates how Life Cycle Assessment (LCA) has been used in order to guide and frame the decision-making processes regarding the selection of "environmentally preferable products" in an ecolabeling scheme. The case study presented is based on the work made by the Ecobilan Group for the European Commission on the European Ecolabel of paints and varnishes.
The risks to fail in determining criteria for selecting such environmentally preferable products is obvious, as other ecolabeling projects have shown. The conflicting interests of the various stakeholders (countries, consumer and environmental associations, and private companies) are numerous enough to lead to the conclusion that setting such criteria is impossible. However, a consensus was built among the working group members.
This shows that a reasonable use of LCA, i.e., accounting both for the power and limitations of the tool, can be crucial in order to:

- rationalize environmental issues, and sometimes challenge generally accepted conventions
- bring confidence to the involved parties (industry, government and associations) in an analytic and transparent methodology, certified by an independent third-party

1. INTRODUCTION

1.1. methodology

The methodology to determine ecolabeling criteria can be divided into five steps:

- ***products and market survey***: this step aims at proposing a classification of products, with particular reference to product use, and taking account of the various aspects likely to introduce a variability into the results of the Life Cycle Inventories (LCI). In particular, it is necessary to define a functional unit to carry out the inventories.
- ***selection of a certain number of specific products deemed representative*** of the market and of environmental issues, for carrying out LCI.
- ***life cycle inventories of the representative selected products***: a materials and energy balance is calculated for the complete life cycle of each selected product from data collected on actual sites.
- ***interpretation*** of the LCI results in terms of main environmental problems, using the currently available scientific knowledge.
  This step is submitted for consideration to the various interested parties (industrialists, ecologists, consumers, public authorities, scientists) who may debate interpretation methods and consider the specific aspects of the ecological problems related to these products.

- ***definition of ecolabeling criteria and thresholds***, based on the results of the life cycle inventories and their interpretation. These criteria are discussed by various interested parties to obtain a multi-criteria label. At this stage, technical and economic aspects are also taken into account.

This procedure is iterative, as the different parties concerned may request an extension to other products or a complementary study on new technologies.

1.2. Ecolabeling Criteria

According to the European council regulation (EEC n° 880/92), articles 4 and 5, three kinds of criteria are distinguished for the ecolabel:

- *ecological criteria*, which are determined according to a global approach (from the cradle to the grave)
- *criteria which refer to general principles* (toxicity, ...)
- *fitness for use criteria*, to ensure that the product should have at least a minimum level of quality

2. DEFINITION OF THE PRODUCT GROUP

According to the European council regulation (EEC n° 880/92, article 3), this definition is based on the function, i.e., the group to be labelled has to contain products fulfilling the same function.

The definition of the product group was agreed as: **"decorative indoor paints and varnishes for professional and do-it-yourself users".**

Included in the field of application:
- paint cans bearing the label "for indoors and outdoors use", because they are at least applicable indoors,
- undercoats for wood and masonry, because they are applicable indoors,
- liquid or paste formulas which have been pre-conditioned or prepared to meet the consumer's needs,
- white-base products intended to be tinted with "tinting" machines at the consumer's request.

Excluded from the field of application of the ecolabel:
- outdoor paints and varnishes for professional and do-it-yourself users,
- paints and varnishes for industrial use,
- primary coats for metal, because they are anti-corrosion products.

The chosen functional unit was to cover 20 m^2 with an opacity of 98%[1].

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1 Nota: durability has not been included in the functional unit because:

- no standardised test method is representative of the ageing of indoors paints. This type of ageing is very different from wheathering outdoors and especially it involves neither photodegradation, which is the most severe agression to paint binders, nor rapid temperature changes.
- Indoors paints generally do not suffer chemical or physical degradation during their normal life span of two to ten years. They are often changed for a question of fashion or taste. The life time is therfore often shorter than the durability

3. THE ENVIRONMENTAL ISSUES IDENTIFIED IN THE LIFE CYCLE OF THE INDOOR DECORATIVE PAINTS

3.1. Modest Aim

After the life cycle inventories have been calculated by Ecobilan (with site-specific data provided by European and American companies) for the eleven representative paints, a lot of detailed figures were available to the ad hoc working group members. These data encompassed about 150 flows (inventory results) and the contribution of each stages in the life cycle. The chosen functional unit for the calculation of the inventories was the quantity of paint needed to cover 20 m^2 with an opacity of 98%[2].
These inventories have been interpreted in order to identify the main environmental problems raised by the life cycle of the products.
Because the label is a **multi-criteria label**, it is **not necessary to establish a hierarchy** of all the flows. However, no scientific and objective way exists to prioritize flows corresponding to different environments (CO_2, CO, NO_x, ..., for air, suspended matter, COD, nitrates, ..., for water, ...).
As a consequence, the aim of the interpretation phase is modest: only to distinguish between main problems and other problems.

The criteria were then determined with relation to each main environmental problem.

3.2. Process to Identify the Main Environmental Problems

The process consists of:

- the regrouping of flows which are linked together,

- a simple hierarchization of environmental problems:
  - main problems,
  - other problems.

The regrouping consists of:

- identifying data which are linked together by their common origin.
  For instance, in some cases, CO_2 and CO emissions come mainly from the electricity production.

- identifying redundant data.
  In the former example, among the CO_2 emissions, the CO emissions and the electricity consumption, two information are redundant because they all vary in the same proportions.

- retaining data which bring new information.
  In the same example, one can keep the CO_2 emissions (because it contributes to environmental impacts such as global warming).

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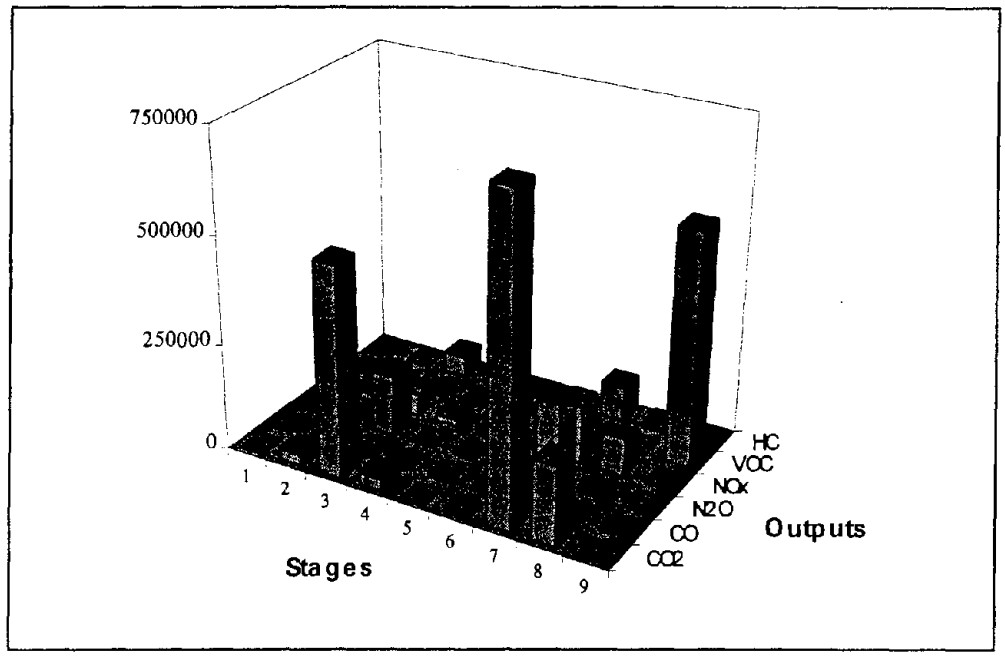
2 Nota: durability has not been included in the functional unit because:

- no standardized test method is representative of the aging of indoor paints. This type of aging is very different from weathering outdoors and especially since it involves neither photodegradation, which is the most severe agression to paint binders, nor rapid temperature changes.

- Indoor paints generally do not suffer chemical or physical degradation during their normal life span of two to ten years. They are often changed for a question of fashion or taste. The life time is therfore often shorter than the durability.

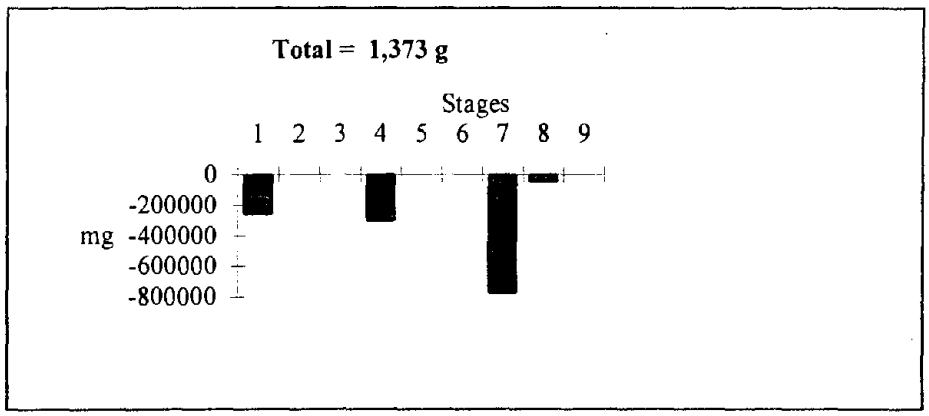
At the same time, the process allows one to:

- identify the main contributors (substances, stages) to a given impact, when a relevant index is available. The use of indices allows one to translate the substances into environmental impacts (non-renewable resources depletion, global warming, atmospheric acidification, eutrophication, etc.), and to appreciate the contribution of each substance to various environmental impacts.



In this example, the stage n°7 constitutes the main contribution to the global warming (in CO_2 equivalent) with the CO_2 emissions.

- identify the main contributors (stages) to the emission of a given substance or to the consumption of a given raw material, in the absence of a relevant index[3].



In this example, the stage n°7 constitutes the main contribution to the particulate matter emissions.

[3] Even when index exists and since the available indices rely on the scientific knowledge which is still under discussion, the interpretation is not limited to the use of these indices.

3.3. The Main Environmental Problems and Their Origin in the Life Cycle of the Paints

In the case of the eleven paints which have been studied, regrouping of data yields the results presenting in the following table and showing the main environmental problems and the stages of the life cycle which constitute the main origin.

Environmental problems	Origin in the life cycle of the paints
Non renewable resources depletion	**Mainly coming from: production of the TiO2, the alkyd resins and the solvents** ***Mainly due to: petroleum consumption***
Global warming	**Mainly coming from: production of energy for TiO2 process, the coke for lithopone process** ***Mainly due to: CO2 emissions***
Atmospheric acidification	**Mainly coming from: TiO2 process** ***Mainly due to: SOx emissions***
Tropospheric ozone creation	**Mainly coming from: application of the paint** ***Mainly due to: VOC emissions***
Other air emissions	**Mainly coming from: production of energy for TiO2 process**
Water consumption	**Mainly coming from: TiO2 process**
Eutrophication	**Mainly coming from: production of the resins and their constituents** ***Mainly due to: COD***
Other discharges into water	**Mainly coming from: TiO2 process, washing of the application tools (brushes, ...)**
Solid waste	**Mainly coming from: application of the paint** ***Mainly due to: can and paint residues***

4. THE SELECTIVITY OF THE ECOLABEL (TARGETS)

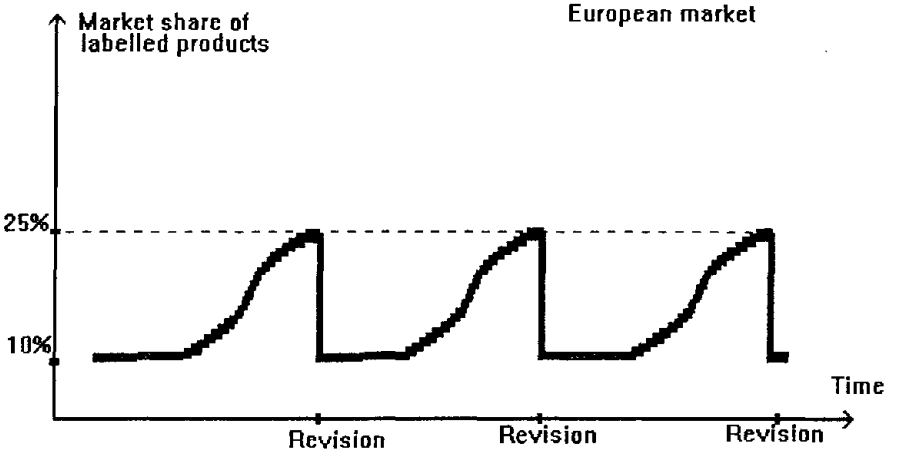
The thresholds of the criteria must be defined in order to obtain an adequate selection in terms of:

- visibility of the label by consumers,
- and encouragement for industrialists to improve their products.

The targets chosen by the ad hoc working group members was that 10 to 15 % (in weight) of paints and varnishes belonging to the product group meet the thresholds on the European market soon after the date of publication of the criteria.

Since the label is a multicriteria label, its selectivity results from the interlacing of its various criteria, and not solely on one of those (e.g. VOC criterion).

As a consequence, the selectivity of each criterion should be calculated and then the global selectivity of the label. Within a few months after the criteria and thresholds are published, the competent bodies will be able to observe the actual selectivity of the thresholds. When selectivity peaks to about 25 %, the European Commission could then revise the label to make the criteria more severe in order to come back to about 10 to 15% labelled products (see figure below).



5. THE ECOLABELING CRITERIA

5.1. The ecological criteria

The ecological criteria are related to the main environmental problems identified in the LCA of the products. In order to allow private companies to easily check the compliance of their products with the criteria, the determination of the criteria from the environmental problems was based on the technical and economical feasibility discussed within the ad hoc working group members.

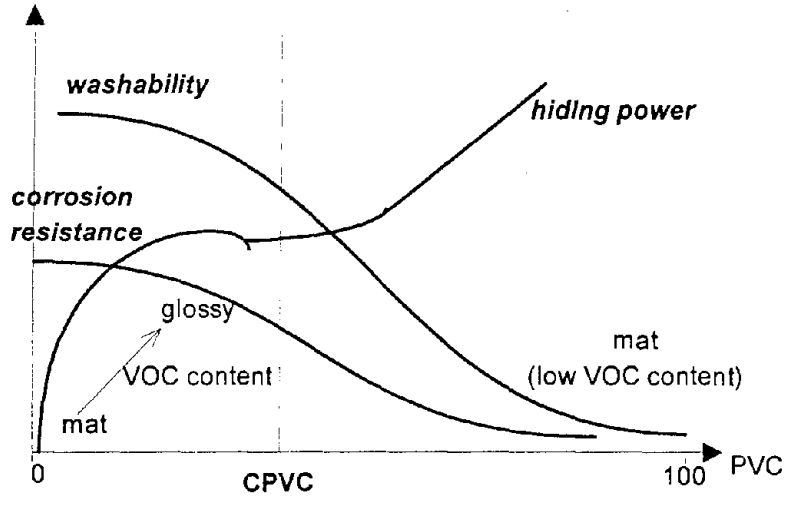
The ecological criteria presented below are thus not directly expressed in terms of environmental problems to be reduced but they pave the way to achieving this aim by referring to the ***key parameters which are at the origin of these main impacts***. For instance, the previous table showed that various environmental problems (non renewable resources depletion, global warming, ...) are mainly due to the production of titanium dioxide. Therefore the proposed criteria are not expressed in terms of reduction of each environmental problem but concerns the optimization of the use of titanium dioxide (see below) which is the driving parameter in that case.

Each criterion is now presented with some justifications coming from the discussions of the ad hoc working group.

5.1.1. Classification of Paints

Community ecolabel requirements on paints and varnishes take into account a classification of paints for criteria n°3 and 4.
This classification is **based on the function** of the paints, and stems from the discussions of the ad hoc working group members about the volatile organic compounds (VOC) content of the paints which have shown that **the VOC content and various characteristics of the paints (washability, gloss, hiding power, corrosion resistance, ...) are closely related through the Pigment Volumic Concentration (PVC).**
This relationship can be roughly represented by the following graph. The purpose of this paragraph is not to give detailed and technical explanations but only to highlight some general conclusions.

The relation between various characteristics of the paints and the PVC



The formula which gives the PVC is:

$$PVC = \frac{Vp}{Vp + Vb} * 100$$

with Vp = Volume of pigments and extenders
Vb = Volume of binder
100 = Volume of the coating

When Vp = 0, i.e. when there is no pigment, PVC = 0.
When Vb = 0, i.e. when the coating is made of solid particles, PVC = 100.
When Vb = 100 - Vp, i.e., when the resin fills the empty areas, PVC reaches the critical PVC: CPVC. Above this value, the paints have a high hiding power, unwashable and mat with a low VOC content. Below this value, they have a lower hiding power, washable and the gloss increases with the VOC content.

The CPVC is therefore the limit point for which characteristics change.
PVC should thus have been a relevant way to classify the paints according to the function. But practically the PVC of a product is difficult to measure.

As a consequence and since gloss is the characteristic of the paints which has the closest relationship to the VOC content (a low VOC content gives a low gloss as shown on the left side and on the right side of the graph and a high VOC content gives a high gloss as shown on the left side of the graph), gloss has been retained to classify the products.

Then the ad hoc working group members have decided to allow a higher level of VOC for glossy products and a lower level of VOC for mat products.

Two classes are thus defined:

Class 1: Paints with a specular gloss below or equal to 40 units at $\alpha = 60°$
Class 2: Paints with a specular gloss above 40 units at $\alpha = 60°$

Remark: There is no need to distinguish between varnishes with regard to VOC content and aromatics content because:

- there is no particular relationship between gloss and VOC content for varnishes,
- additives (and thus not VOC) are used in low quantities in order to obtain mat varnishes (fumed silica and waxes).

5.1.2. Criterion n° 1: Information to the End User

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
1	Information on criteria relevance	All	Existence of the recommended wordings on can		Checking by Competent body (verification on white basis and coloured products in the same range)

For instance: "This product complies with the requirements of the European Union ecolabel for indoor paints with gloss below 40 units".

5.1.3. Criteria n° 2 and n° 3: White pigments

In order to address non-renewable resources depletion, global warming, atmospheric acidification, other air emissions, water consumption, discharges into water (see table in section 3.3)

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
2	White pigments content*	Paints	<40 g/m² . g of white pigment* . m² of dry film with 98% opacity**	Producer's declaration	Checking by competent body on white basis only
3	TiO2 production	Paints	To comply with directive on TiO2 (CEE N°92/112)	Producer's declaration	Checking by competent body

The table in section 3.3 showed that:

- titanium dioxide process (either the production of the raw materials or the production of the energy consumed during the process) is the main contributor to various environmental impacts: non renewable resources depletion, global warming, atmospheric acidification, other air emissions, water consumption, discharges into water.
- lithopone process is also a main contributor to global warming.

To address these various environmental impacts at the same time, both criteria are related to the key parameters: the white pigment content and the process.

The criterion n°2 applies to all types of white pigments usually used for the product group: titanium dioxide (TiO_2), lithopone, etc.
One can notice that **this criterion is related to the functional unit** used in the LCAs.

The criterion n° 3 applies wherever the TiO_2 production plant is located, i.e., not only in Europe where the compliance with the directive is already necessary but also in other countries, and to whatever process is used (sulfate or chloride).

● Selectivity of criterion n°2

The selectivity of the TiO_2 content requirement (below 40 g/m^2 with 98% opacity) is as follows:

- about 50% (in liters) of the water based paints comply with this requirement;
- about 80% (in liters) of the solvent based paints comply with this requirement.

5.1.4. Criterion n° 4: Volatile Organic Compounds Content

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
4A	VOC content	Class 1 paints	<30 g/l minus water	Calculation and results provided by the producer	Checking by competent body (verification on the white basis and coloured product in the same range)
4B	VOC content	Varnishes and class 2 paints	<250 g/l minus water		

These volatile organic compounds correspond to the solvents contained in the paints, the resins and the additives.

Due to the lack of a standardized definition, the following definition is proposed:
"any organic compound with, at normal conditions for pressure, a boiling point (or initial boiling point) lower than or equal to 250°C".

The table in section 3.3 shows that VOC emissions during the application of the paint or the varnishes by the consumer is the main contributor to the tropospheric ozone formation.
To address this environmental impact, the ad hoc working group members have identified the key parameter being the VOC content.

As explained above (criterion n°1), the VOC content of a paint increases with the gloss and two classes of paints have been defined corresponding to two functions characterized by the specular gloss:

- the class 1 paints, which are mat, mat-satin or satin and which can have a low VOC content,

- the class 2 paints, which are semi-glossy, glossy or high glossy and which have generally a high VOC content.

The thresholds have then been determined according to selectivity considerations (see below). The threshold for class 2 paints has also been chosen in order that the high solid solvent paints could be awarded the label, because the Life Cycle Inventories have shown that the high solid paints have lesser impacts on the environment than other technologies when the functional unit is considered.

Calculation of the VOC content:

The VOC content calculation will have to take into account:
- solvents voluntarily added by the manufacturer,
- coalescing agents and co-solvents falling under VOC definition (see below),
- VOC content of resins solutions or emulsions,
- solvents known by paint manufacturer (solvents in additives, etc...)
- solvents recommended for product dilution by the applicant (in accordance with the instructions on the packaging),

according to the following formulas:

$$\textit{VOC (in g/l minus water)} = \frac{\text{total amount of VOC (in g)}}{\text{total volume of product (in l) - total water content (in l)}}$$

or

$$\textit{VOC (in g/l minus water)} = \frac{\text{total amount of VOC (in g)}}{\frac{\text{total amount of product (in g)}}{\text{density}} - \text{total water content (in l)}}$$

This leaves out minor amounts of VOC coming from additives of unknown composition.

Example of calculation

	Solvent based formulation
Solid resin form a polymer emulsion (in % w/w)	32
Pigments (in % w/w)	22
Extenders (in % w/w)	3
Coalescing agent (in % w/w)	7
Water (in % w/w)	36
Total (in % w/w)	100
Density kg/l	1.3
total amount of VOC (in g)	7*1300/100 = 91
total amount of product (in l)	1.0
total water content (in l)	36*1300/100/1000 = 0.468
VOC g/l minus water	91/(1.0-0.468) = **171**

Today, the varnish technology is mainly solvent based. This explains the fact that the same threshold has been retained for the varnishes and the class 2 paints.

- Selectivity of the criterion n°4

- about 12.9% (in weight) of class 1 European paints comply with the requirement 4A;
- about 3.1% (in weight) of class 2 European paints comply with the requirement 4B;
- therefore, about 16% (in weight) of European paints comply with the requirement 4.

5.1.5. Criterion n° 5: Volatile Aromatic Hydrocarbons Content

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
5A	Volatile aromatic hydrocarbons content*	Class 1 paints	<0.5% w/w of product	Calculation and results provided by the producer	Checking by competent body (verification on white basis and coloured products in the same range)
5B	Volatile aromatic hydrocarbons content*	Varnishes and class 2 paints	<1.5% w/w of product		

This criterion has been defined in order to address the impact on the environment due to the VOC emissions into the atmosphere.
At first, the members of the working group wanted to use the POCP index (Photochemical Ozone Creation Potential) to weight the impact of each solvent. But, on the basis of currently accepted scientific knowledge, it appeared that this index was not reliable enough. The members agreed to determine a specific criterion for the aromatics content.
The ad hoc working group also decided to have different aromatic thresholds for the two classes in order to allow high solid solvent paints to be labelled (see above criterion n° 4B).
In fact, the difference one can notice between the two thresholds are not so important when one reasons in terms of functional unit. This is due to the high performance of the high solid technology: the quantity of paint necessary to ensure a given opacity is much lower than for a class 1 paint.

Example of calculation	High solid paint (class 2)	Water borne paint (class 1)
Average hiding power (m^2/l)	20	7
Average density(kg/l)	1.0	1.0
Aromatics content (% w/w of product)	1.5	0.5
Quantity of aromatics per functional unit (g/m^2)	7.5	7.1

It was not possible to assess the selectivity of this criterion with precision but according to paints manufacturers, the selectivity is not very important (i.e., this criterion is not very drastic) except that to be awarded the label a product should not contain traditional white spirit with 17-18% of aromatics.

5.1.6. Criterion n° 6: Water Pollution

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
6	Effluents from application tools cleaning	All	Existence on can of recommendations concerning cleaning of tools*		Checking by competent body (verification on white basis and coloured product in the same range)

The LCAs have shown that the cleaning of the application tools was the main contribution to water impacts. Due to important variations between the consumer's behaviors (between the different countries in Europe, and even within the same country), it was irrelevant to define a quantitative criterion.
A qualitative criterion has therefore been defined concerning consumer's information. The recommendation should be adapted by the manufacturer to the type of product.
Examples of such recommendations are given below:

- for solvent based products: 'solvent used for cleaning should be stored and used for later painting operations';
- for water based products: 'remove excess product from tools before cleaning them'.

5.1.7. Criterion n° 7: Solid Waste

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
7	Solid waste - can and paint residues	All	Existence of recommendations on can explaining how to preserve product in can after opening*		Checking by competent body (verification on white basis and coloured product in the same range)

The LCAs have shown that the application of the product by the consumer is the step in the life cycle which produces the highest quantity of solid waste (paint residues in the can and the can itself).
Waste management differs according to the countries in Europe; this criterion is thus only a qualitative one and concerns consumer's information. The recommendation is intended to be adapted by the manufacturer to the type of product and packaging.

5.2. The General Principles Criteria

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
8	Coloured pigments and other substances	All	No use of substances based on: . cadmium . lead . chromium VI . mercury . arsenic	Producer's declaration	Checking by competent body (verification on white basis and coloured product in the same range)
9	Dangerous substances	All	No use of substances which are (EEC 67/548): . very toxic . toxic . carcinogenic . mutagenic . toxic for reproduction	- Producer's declaration - Safety data for all components used in the formulation provided by the producer	Checking by competent body (verification on white basis and coloured product in the same range)
10	Dangerous preparations	All	No hazardous classification with the exception of R10	Producer's declaration	Checking by competent body (verification on white basis and coloured product in the same range)

R10 is the risk sentence associated with flammable preparations having a flash point higher than 21°C (ambient temperature) and lower or equal to 55°C and sustaining combustion. Since this sentence does not require the flame symbol on the label according to directive EEC/67/548, products bearing this sentence on the can comply with the criterion.

5.3. The Fitness for Use Criteria

N°	Criterion	Applicable to	Requirement	Means of proof	Compliance verification
11A	Fitness for use	Paints	Hiding power >7 m²/l	ISO 6504/1	Test report (test performed only on white basis product)
11B	Fitness for use	Varnishes	Satisfactory resistance to liquid required for water during one hour at ambient temperature	ISO 2812/1 - method 3	Test report

- Selectivity of criterion n°11A:

- about 30% (in liters) of the water based paints comply with this requirement,
- about 80% (in liters) of the solvent based paints comply with this requirement.

- Selectivity of criteria n° 2 and n°11A taken together:

- about 10% (in liters) of the water based paints comply with these two requirements,
- about 50% (in liters) of the solvent based paints comply with these two requirements.

6. THE SELECTIVITY OF THE ECOLABEL (ASSESSMENT FROM CRITERIA)

As shown previously, the ad hoc group has been able to assess the selectivity of various criteria thanks to figures coming from manufacturers. It was not possible to calculate the selectivity of each criterion due to a lack of necessary data. This relative lack of information has its source in the industry not being used to work with these new criteria.

Therefore the following procedure has been used:

- the objective of the working group members was that the global selectivity of the label reaches about 10 to 15 % (in weight) soon after the publication of the criteria.
- the selectivity has been assessed for three main criteria (white pigment content criterion, VOC criterion and fitness for use criterion) by the means of specific figures provided by titanium dioxide and paints manufacturers.

The following table summarizes the selectivity for the criteria:

Criteria	Assessed selectivity (% of products complying with the requirements at the European scale)
Criterion n° 2: White pigment content	about 50% (in liters) of the water based paints about 80% (in liters) of the solvent based paints
Criterion n° 4: VOC content	about 12.9% (in weight) of class 1 paints about 3.1% (in weight) of class 2 paints therefore about 16% (in weight) of paints
Criterion n°11A: Fitness for use for paints	about 30% (in liters) of the water based paints about 80% (in liters) of the solvent based paints
Criteria n° 2 and n° 11A taken together	about 10% (in liters) of the water based paints about 50% (in liters) of the solvent based paints

At least, the global selectivity will be lower than the lowest selectivity among the criteria. This lowest selectivity is 16 % in weight (for VOC criteria).

As a conclusion, the ad hoc working group has estimated that about 10 to 15% of the products may actually be labelled.

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OPTIMIZING COATING FORMULATIONS FOR TOTAL ENVIRONMENTAL AND PRODUCT PERFORMANCE

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EXECUTIVE SUMMARY

Organic solvents have been used for hundreds of years in virtually all types of paints and coatings. Although waterborne and other alternative coating technologies have begun to replace solvent-based coatings in certain applications, solvent-based coatings are still used in the vast majority of coating operations.

Most organic solvents are volatile organic compounds (VOCs) and can react photochemically in the atmosphere to form ground-level ozone. As a result, policy makers have encouraged -- and in some cases required -- the use of low- or no-VOC coatings. This paper points out that VOC content should be only one of the factors considered by users, formulators, and regulators when evaluating alternative coating systems.

In some cases, there is no appreciable environmental benefit to be gained from reducing solvent emissions. Recent reports by the National Academy of Sciences and by the U.S. Environmental Protection Agency have shown that, in areas where there are relatively low levels of nitrogen oxides (NO_x), reducing VOC emissions will have little or no effect on reducing ground-level ozone.

In addition, regulatory or voluntary programs to control VOC emissions from coatings should take seasonal and temperature differences into account. Because of the atmospheric chemistry of ozone formation, there is little or nothing to be gained from using low-VOC coatings during the winter months or in the cooler parts of the country. Moreover, the ozone-formation potential of different VOCs varies depending on their photochemical reactivity. Therefore, where VOC-control efforts are justified, they should focus on VOCs with the highest photochemical reactivity.

Coating users and formulators, as well as regulators, should also consider performance tradeoffs when evaluating low- or no-VOC coating technologies. For technical reasons, alternative coating technologies are difficult or impossible to use under certain circumstances. For example, water-based technologies may not be feasible in areas with high relative humidity or desirable for applications involving frequent touch-up.

The use of low-VOC coatings may also involve significant environmental tradeoffs. In many cases, for example, water-based coatings generate increased levels of liquid and solid wastes. In addition, because water has a very high heat of vaporization, water-based systems often require much more energy usage than solvent-based systems.

Life Cycle Assessment (LCA) is a useful analytical tool for comparing the environmental tradeoffs associated with the use of alternative coating technologies. Two recent studies using LCA have shown that water-based systems are not necessarily environmentally beneficial when compared to traditional solvent-based systems. Because no coating technology is always environmentally preferable, regulatory programs should be designed to encourage advances in all coating technologies.

INTRODUCTION

Organic solvents have been used for hundreds of years in virtually all types of paints and coatings. In recent years, waterborne and other alternative coating technologies have begun to replace solvent-based coatings in certain applications. However, with the exception of architectural coating applications -- where waterborne products are now widely used -- solvent-based coatings are still used in the vast majority of coating operations.

Most organic solvents are volatile organic compounds (VOCs), which can react photochemically in the atmosphere to form ground-level ozone. Ground-level ozone is the main component of "smog," which continues to be a health and environmental concern in some areas in spite of the progress that has been made in controlling it over the last 20 years. Although VOC emissions from coatings represent a relatively minor portion of total VOC emissions, industry and regulators have recognized the need to focus on all emissions that may contribute to ozone formation.

As part of a national effort to reduce ground-level ozone and maintain it within acceptable levels, the U.S. Environmental Protection Agency (EPA) and other regulatory agencies have encouraged -- and in some cases required -- the use of low- or no-VOC coatings. The use of such products, however, usually involves certain tradeoffs. This paper points out that the VOC content of a coating should be only one of the factors considered by users, formulators, and regulators when evaluating low- or no-VOC coating technologies.

In most cases, a switch from a traditional solventborne coating to an alternative coating technology imposes a direct financial cost (and frequently an indirect performance penalty) on the user of the coating -- a cost that is then passed along, at least in part, to the ultimate consumer of the coated product. Although these costs can be significant and should not be overlooked, they are not the focus of this paper. Rather, this paper examines the other tradeoffs that are associated with alternative coating technologies.

These tradeoffs -- whether measured in terms of direct financial costs or otherwise -- should be compared with the benefits of switching to a low- or no-VOC coating. Historically, these benefits have been measured by the tons of VOC emissions that would be eliminated by such a switch. As the National Academy of Sciences (NAS) emphasized in a recent report, however, reducing VOC emissions does not always benefit the environment. In some cases, VOC emissions have little or no impact on ground-level ozone. Regulatory efforts should focus on the purpose for which VOC emission are of concern -- ground-level ozone -- and not on VOC emissions alone.

Thus, when evaluating low- or no-VOC coating technologies, it is important to consider the environmental benefits that they will provide and the environmental and performance tradeoffs that are associated with such technologies. This paper first briefly reviews the benefit side of this equation, outlining the conditions under which low- or no-

VOC coatings may be desirable. It then reviews the tradeoffs that companies and regulatory agencies should consider when evaluating low- and no-VOC coating technologies.

ASSESSING THE ENVIRONMENTAL BENEFITS OF CONTROLLING VOC EMISSIONS FROM SOLVENTS

Unlike most other regulated pollutants, ozone is not emitted directly into the air from man-made sources. Rather, it is a so-called "secondary pollutant" that is formed by the interaction of a broad mixture of natural and man-made emissions (known generally as ozone precursors) in the presence of sunlight. To the extent possible, regulators and users should take into account the complexities of the process by which ozone is formed. Otherwise, significant resources will be spent on coating technologies that have little or no impact on reducing ozone formation.

The Respective Roles of VOCs and NOx

Although carbon monoxide plays a small role in ozone formation, the most important ozone precursors are VOCs and oxides of nitrogen (NOx). There are several significant sources of VOC emissions, including natural or "biogenic" sources such as trees and vegetation and man-made sources such as vehicle emissions, petroleum refining and distribution, and combustion sources. As noted above, organic solvents, including solvents used in coating applications, are also a source of VOC emissions.

For many years, EPA has emphasized reductions in VOC emissions as the primary approach for controlling ozone. In December 1991, however, the National Academy of Sciences issued a report entitled *Rethinking the Ozone Problem in Urban and Regional Air Pollution*.[1] Among other things, the NAS report questioned the regulatory focus on VOC emissions, noting that ozone is formed only if there is the right atmospheric mixture of VOCs and NOx. The report concluded that, in many areas, reductions in VOC emissions would have little or no effect on ozone levels, and that in a few cases, such reductions would actually be counterproductive and lead to increased ozone levels.

In July 1993, EPA submitted a report to Congress entitled *The Role of Ozone Precursors in Tropospheric Ozone Formation and Control*, which responded to the NAS report.[2] This report, which was required under section 185B of the 1990 Amendments to the Clean Air Act, largely agreed with the conclusions of the NAS study. It noted that, in some areas, efforts to reduce ozone levels should continue to focus primarily on VOC emissions. The report acknowledged, however, that in many areas of the country, only NOx reductions will have a significant effect on reducing ozone levels, and that regional modeling will be required to identify the type and amount of emissions reductions that will be necessary to bring specific areas into attainment with national ambient ozone standards.

Low- and no-VOC coatings may be a desirable option in areas that need to reduce VOC emissions in order to reach attainment with ambient standards. However, in areas that

are "NOx-limited" -- i.e., where VOC emissions have little or no effect on ozone levels -- regulatory efforts should be focused on reducing NOx emissions. Any program aimed at reducing solvent emissions in these areas would impose unnecessary costs on businesses and consumers.

The Role of Sunlight and Temperature

In most parts of the country, high ozone levels are a concern only during the summer, when higher temperatures increase the rate at which NOx and VOCs react in the atmosphere to form ozone. The Clean Air Act recognizes this fact by requiring EPA, under certain programs, to make a distinction between the "high ozone period" (the summertime) and the rest of the year. For example, during the summer months, gasoline sold in some urban areas must be reformulated to reduce VOC emissions from vehicles by at least 15 percent.

In addition to making a distinction between summer and winter, EPA has recognized that hotter areas of the country may require different VOC controls than cooler areas. For example, EPA has set a more stringent evaporative standard for gasoline sold in certain southern cities that, on average, experience higher summertime temperatures than the rest of the country.

Regulatory programs to control VOC emissions from coating operations should also take seasonal and temperature differences into account. Little or nothing is gained from using low- or no-VOC coatings during the winter months or in the cooler parts of the country. EPA already has recognized that it is appropriate to impose different requirements for coatings depending on the time of year during which they are applied. In the regulatory negotiation on Architectural and Industrial Maintenance coatings (the so-called "AIM Reg Neg"), the Agency agreed to propose different VOC limits for traffic paints depending on whether they are applied during the summer or during the winter. For many solvent users, a time-of-year restriction could easily be enforced by including it in their operating permit.

The Importance of Taking Reactivity into Account

Different VOCs (including different solvents) are not equal in their potential to create ground-level ozone. For many years, EPA has recognized that the potential contribution that each individual VOC makes to ozone formation depends on its photochemical reactivity. Assuming that there are sufficient amounts of NOx and sunlight, VOCs with the highest reactivity cause the most ozone. Therefore, from the standpoint of environmental protection, reductions of high reactivity VOCs are more valuable than reductions of lower reactivity compounds.

In recognition of this fact, EPA has developed a list of compounds that have only "negligible" reactivity. These compounds are exempt from regulation as VOCs. Except for these exempt compounds, however, federal and state regulations generally treat all VOCs as though they had the same impact on ozone formation. Unfortunately, this approach does not

create any incentive for companies to focus on reducing emissions of highly reactive VOCs that have the greatest impact on ozone formation.

Over the last several years, researchers have begun to develop methods for weighting the photochemical reactivity of various VOCs, and it is now possible to develop regulatory programs based on reactivity indices or scales.[3] The State of California has already developed a reactivity-based program for reformulated gasoline that places different weights on individual VOCs. Because the relative reactivity of different VOCs varies depending on NOx conditions and other factors, none of these indices is perfect for all conditions. From an environmental perspective, however, virtually any of them would be preferable to the current regulatory approach, which treats VOCs as though they were all equal.

Additional data may be needed before a reactivity-based approach can be used for regulating solvent emissions from coatings. However, both regulators and users should have a strong incentive for developing and supporting such an approach. A reactivity-based system would be much more effective at reducing ozone levels than the current approach and would do so in a more cost-effective manner.

Such an approach would recognize that lowering the VOC content of a coating does not necessarily reduce its ability to form ozone -- even assuming that it is used in an area that is not NOx-limited. A coating that uses less solvent may not offer an environmental advantage over a traditional coating if the solvent in the low-VOC coating has higher photochemical reactivity. Thus, in order to evaluate the benefits of switching to a low-VOC coating, the reactivity of its solvent must be compared to the reactivity of the solvent it would replace.

TRADEOFFS ASSOCIATED WITH LOW- AND NO-VOC COATINGS

When considering the total environmental and product performance of a coating, its VOC content is only one of many factors that should be considered. Some of the factors are technical, and may appear to be of interest only to formulators and users. Many of these technical factors, however, have a significant (although sometimes indirect) effect on the environment and should also be of interest to regulators.

By the same token, users and formulators should be aware of collateral environmental impacts associated with different low- and no-VOC coatings. These impacts not only affect the environment, but may also trigger new regulatory requirements of which the user must be aware.

Technical Considerations

Formulators must balance a number of performance factors in order to develop acceptable formulations of paints and other coatings. Some of these criteria are relevant primarily for specific applications. For example, lacquers require careful attention to blush

resistance, and electrical conductivity is a key factor for electrocoating and electrostatic spray applications. Most factors, however, are relevant for a wide range of coatings. A formulator must generally consider the following key criteria when selecting solvents for a coating formulation: evaporation rate, flash point, resin solubility, surface tension, viscosity, and miscibility with other solvents and diluents.

The first factor to be considered is the relative evaporation rate of the solvents in the coating, which in turn can affect each of the other criteria listed above. In particular, evaporation rate can affect both drying time and resin solubility and must be suitable for the application method. Spray-applied coatings are formulated with fast evaporating solvent blends for fast drying and minimal sags and runs, while brush applied coatings use slower evaporating solvents for longer open time and smooth flowout. Solvent composition changes as evaporation proceeds, and it is important to manage the changing composition to maintain solvency and avoid resin precipitation. If the strong active solvent evaporates too quickly, the blend becomes richer in diluent and the resin becomes insoluble.

Similarly, changes in solvent composition may affect surface tension, viscosity, blush resistance, and miscibility and can result in a variety of other performance problems, including poor leveling, reduced gloss, and other film defects such as "orange peel" and "fish eyes."

Although it is a challenge to balance these various factors in the formulation of solvent-based coatings, it is significantly more difficult to strike the proper balance with lower VOC coatings. Because they have lower solvent content, low- and no-VOC coating formulations are less forgiving in design, and more demanding of application conditions. The following sections describe several important issues to consider when evaluating alternative coating technologies.

Application under Difficult Conditions. For waterborne coatings, one of the most difficult challenges is application under conditions of high humidity. As noted above, evaporation rate is a key factor in the performance of virtually all coatings. With solvent-based systems, the evaporation rate is controlled simply by adjusting the solvent mixture. For waterborne coatings, however, the evaporation rate is a function of temperature and, in particular, relative humidity. As relative humidity increases, the evaporation rate slows. Obviously, at 100 percent relative humidity, where the ambient air is fully saturated, there is no evaporation at all and a water-based coating will not dry.

In order to achieve consistent performance with a waterborne coating, the applicator must control the heat and humidity in the drying area. Controlling these factors is possible for enclosed coatings operations, but often requires significant energy usage, which increases costs and gives rise to collateral environmental impacts associated with energy production and consumption. For some applications (such as aerospace and ship coating and the coating of exterior structures), humidity and temperature control is simply not a feasible option.

The South Coast Basin in southern California has the most severe ozone nonattainment problem of any area in the United States. Because of its relatively constant temperatures and low humidity, it also has an ideal climate for the use of waterborne coatings. Because of the severity of the ozone problem in the South Coast, local regulations have required many coating operations to switch from solvent-based to water-based coatings. Due in large part to the Southern California climate, most of these switches have been successful. Even in the South Coast, however, there continue to be performance and application problems with waterborne technologies. When considering the potential for similar technologies to be used elsewhere, solvent users and regulators must take into account the conditions under which they will be applied. A coating that gives good performance year around in California or Arizona may simply not work during the summer in Mississippi or Louisiana or during the winter in New York.

Technical Performance Issues. Solvent-based coatings have other technical advantages that, in certain applications, make them difficult to replace with alternative coating technologies. For example, although waterborne coatings can be used in some wood finishing applications, such coatings generally cannot be used for the initial coat (the base coat or wash coat) that is applied to the wood. Because wood absorbs water, the application of a waterborne base coat actually raises small wood particles on the surface of the wood. This problem -- known as "grain raising" -- is avoided with solvent-based coatings.

In some cases, the technical advantages of a solvent-based coating also give the coating an environmental advantage when compared to alternative technologies. Again, the coating of wood furniture offers an example. Regardless of the type of coating used, the finish can be damaged during shipping or after the piece of furniture is placed into use. Traditional nitrocellulose lacquers are easily repaired. The solvent in the touch-up coating actually dissolves the existing finish coat and allows the new resin to bind with the old. This makes it simple, for example, to touch up even a very visible spot on the top of a table. In contrast, when alternative coatings are used, the entire table top must be refinished. This is not only more costly, but increases waste generation and requires the use of more coating to cover a greater area. Even if the newer coating has a lower VOC content, the overall emissions are likely to be higher when touch-up is considered because of the increased amount of coating that must be used.

A similar issue arises in autobody refinishing. Using a solvent-based system, a small blemish on a car body can be touched up. With an alternative technology, however, the whole component (such as the hood or fender) must be refinished. Color-matching is also much easier with solventborne systems. Where the color match is particularly sensitive, the use of an alternative coating may require that the entire car be repainted. Such a result is clearly not desirable either from a cost or an environmental perspective.

"Crab trap" effect. For most businesses with coating operations, a switch to an alternative coating technology requires a significant up-front capital investment. Because water-based systems require the use of corrosion resistant components, a company must often replace

existing tanks and piping with stainless steel at the same time it purchases new spray guns and baking ovens. Powder coatings require new spray guns and coating handling machinery, and a company that moves to UV cure or an electron beam curing system must completely replace its existing equipment.

In many cases, the investment in capital equipment will have the practical effect of locking companies into new technologies with which they have little or no experience. Thus, to many solvent users, the alternative technology looks like a crab trap, which lets them in but will not let them out. Although this may not be a major issue for industries with stable product lines, it represents a significant concern for industries that need to change the appearance of their products to respond to customer demands and changes in the marketplace.

Environmental Tradeoffs

Over the last decade, policy makers have learned that a regulatory strategy designed to address one environmental problem may inadvertently create other environmental problems. Often there are cross-media effects, where efforts to reduce pollution in one media increase pollution in another. For example, treating polluted wastewater may generate hazardous sludge, and incineration of the sludge may generate hazardous air pollutants.

Even within the same media, efforts to address one problem may give rise to another. In the early 1970s, for example, regulatory efforts to reduce VOC emissions lead many companies to replace traditional organic solvents with chlorinated solvents, which were later determined to play a major role in depleting stratospheric ozone. In light of this history, regulatory agencies and solvent users should not focus only on VOC emissions. Instead, they should evaluate the full range of environmental impacts.

Waste Generation. Like most industrial operations, coating operations generate both liquid and solid waste. In a typical coating operation, waste is generated at various points in the process. Spray booths or other collection devices for overspray must be cleaned on a regular basis; piping and spray lines must be drained and flushed whenever color or formulation changes are made; and empty shipping containers must be cleaned prior to disposal or reconditioning. In addition, in most operations, some percentage of the coated product must be stripped and recoated because of flaws in the finish -- a process that generates waste in the form of sludge and spent stripping agent. Thus, among other things, the "reject rate" has an impact on the generation of both liquid and solid waste.

Solvent-based systems offer significant advantages with respect to the handling of liquid wastes. The solvent used to clean containers, spray lines, and piping is typically reused several times before it is disposed of by incineration or used as a supplemental fuel. Solvent recovery through recycling may also be attractive -- for both environmental and economic reasons. In that case, the solvents are recovered through distillation and then

reused. Using standard collection procedures, solvent losses are minimal and waste disposal costs are relatively low.

For water-based systems, disposal of liquid waste is more problematic and costly. Aqueous wastes consist mostly of water and suspended pigment and resin particles and soluble organics, with only small amounts of volatile solvents. Liquid waste from the cleaning of containers, spray lines, and piping cannot be reused. Because of the low energy content, liquid waste from a water-based system cannot be incinerated or used as supplemental fuel; and because of the high water content, distillation is usually not a practical alternative. Instead, it must be disposed of as wastewater. In most cases this requires pretreatment, which increases costs and often triggers permit requirements.

In many applications, water-based coating systems also generate increased amounts of solid waste compared to traditional solvent-based systems. Metal coating operations often use electrocoating or electrostatic spray techniques that minimize overspray and therefore increase transfer efficiency. It is significantly easier to manage the electrical conductivity for solvent-based systems than for water-based systems. Therefore, electrocoating and electrostatic spray techniques are more efficient with solvent-based systems. This not only has implications for air emissions, but also means that the solvent-based systems will generate less overspray that must eventually be disposed of as liquid or solid waste.

In addition, water-based coatings have a shorter pot-life than solvent-based coatings. Although this problem can be managed, it cannot be eliminated entirely. As a result, with water-based systems, a higher percentage of unused coating must be disposed of as solid waste.

Finally, as noted above, solvent-based systems are more forgiving than alternative coating technologies for most applications. Among other things, this means that reject rates tend to be lower, on average, for solvent-based systems. Because rejected products must either be disposed of or stripped and recoated, a higher reject rate has several negative environmental consequences. First, of course, it means that additional energy and materials are needed either to recoat the rejected product or to manufacture and coat a replacement product. In addition, an increase in the reject rate increases the generation of liquid and solid waste.

Energy Consumption. As noted above, the use of waterborne coatings may require special attention to humidity control, which leads to increases in energy consumption. Even where humidity is not a major factor, however, many industrial coatings are baked to increase line speed. Because water has a very high heat of vaporization, water-based systems require much more energy to bake than do traditional solvent-based systems. In addition, although water-based systems generate some VOC emissions, the concentrations are usually not high enough to support efficient combustion in afterburners or incinerators. In contrast, solvent-based systems produce vapor concentrations that are sufficiently high to serve as a supplemental fuel source in the baking operation. Therefore, for several reasons, water-

based coatings are likely to consume more energy than solvent-based systems. Policy makers should not overlook the environmental consequences of energy consumption when evaluating the overall impact of different coating technologies.

The Tradeoff Between HAP and VOC Emissions. When evaluating the full range of environmental issues related to paints and coatings, it is also important to consider the tradeoff between VOC emissions and emissions of substances listed as "hazardous air pollutants" (HAPs) under the federal Clean Air Act. Two of the solvents on the HAPs list, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), are very efficient solvents and, therefore, are especially valuable in the formulation of high solids coatings. Not only do they dissolve a wide variety of resins, but compared to the available non-ketone alternatives, they require a smaller amount of solvent to perform the same function. Thus, the use of MEK and MIBK allows the formulation of coatings with higher solids and lower solvent emissions. For this reason, the use of MEK and MIBK can *reduce* VOC emissions from many coating operations.

In a recent rulemaking to regulate coatings used in the shipbuilding industry, EPA specifically addressed this issue, noting that a coating reformulated to reduce its HAP content may have "higher VOC content than the one it replaces." 59 Fed. Reg. 62681, 62688 (Dec. 6, 1994).[4] The Agency goes on to state that "the HAP to VOC ratio may even increase when a company develops a new reformulation with lower VOC." *Id.* It also notes that, even where the HAP to VOC ratio in the coating increases, "the absolute HAP *emissions* are likely to go down," presumably because higher solids coatings allow more coverage per gallon of coating. *Id.* (emphasis added).

In recognition of this tradeoff, the proposed rule for the shipbuilding industry includes coating content standards that are identical for HAPs and VOCs. This approach encourages the use of higher solids coatings and eliminates the incentive for formulators to use less efficient solvents that must be used in greater volumes.

By effectively encouraging the use of certain solvents that are listed as HAPs, the proposed rule also implicitly recognizes a fact that EPA has explicitly acknowledged in other rulemakings: that certain solvents listed as HAPs have relatively low toxicity. Unfortunately, there are many in the public -- and even some solvent users and regulators -- who do not understand that the list of HAPs includes substances with a wide range of hazard characteristics, including a few such as MEK and MIBK that have low toxicity. Regulators, chemical users, and the public should understand that, in terms of their potential hazard, all HAPs are not equal.

In order to understand the relative toxicity of various chemicals, it is helpful to refer to EPA's recent proposed rule under section 112(g) of the Clean Air Act, which shows that MEK and MIBK are among the HAPs with the lowest toxicity. 59 Fed. Reg. 15,504 (April 1, 1994).[5] More importantly, the proposed rule also contains an EPA model for calculating the amount of a chemical that may be emitted into the ambient air without posing more than

a trivial risk to human health or the environment. Even using conservative assumptions, this model suggests that a typical facility could emit **2000 tons per year** of MEK and **1500 tons per year** of MIBK and still pose only a trivial risk.

This analysis is not used to suggest that a facility should be allowed to emit these quantities without triggering regulatory requirements. It is simply intended to show that MEK and MIBK pose very little hazard -- even though they are listed as "hazardous air pollutants." Thus, reformulating a coating to reduce emissions of MEK or MIBK is likely to increase emissions of VOCs without providing any benefit in terms of risk reduction. This tradeoff again illustrates the importance of considering all relevant factors instead of focusing solely on low-VOC or low-HAP content.

The Role of Product Performance. This paper does not attempt to review the data comparing the performance of various coating technologies in different applications. It must be noted, however, that product performance is an important factor that cannot be overlooked when evaluating the overall environmental impact of a coating system.

Long experience in using solvents has allowed product formulators to achieve important performance attributes across a broad range of coating applications. In some cases, a switch to low- or no-VOC coatings may reduce product performance and undermine environmental objectives (in addition to increasing costs). For example, a paint formulator may be able to reduce the VOC content of an industrial coating by 25 percent, but in the process might produce a product that lasts only half as long. Because the user would have to repaint twice as often, the overall VOC emissions would increase, not decrease, over the long run.

Life-Cycle Assessments

As discussed above, a decision to switch from a traditional solventborne system to a low-VOC coating technology is likely to involve a number of environmental tradeoffs and has implications for all environmental media, not simply for ground-level ozone. The environmental tradeoffs and multi-media effects of different techniques for achieving environmental goals can be compared through the use of life cycle assessment (LCA), which allow a rigorous analysis of environmental impacts both upstream and downstream from the regulated product or process. These consequences can be compared using LCA techniques, which consider such factors as:

- raw materials input
- energy input
- solid waste generated
- emissions to air
- releases to water
- other environmental releases
- amount of usable product
- product life

These individual impacts are affected by the respective production-use-disposal chain for each option considered. The various factors discussed above, including the amount of coating required per unit of production, refinish and reject rates, and durability of the finished coating can all influence the overall environmental impact of each option. As with other analytical tools, LCA does not necessarily provide absolute precision. Nevertheless, it is a useful tool for comparing the entire range of environmental issues associated with different approaches for addressing environmental concerns.

Over the past few years, at least two comprehensive life-cycle assessments have been conducted to compare the overall environmental impact of different coatings technologies. A 1992 study conducted by the Eindhoven University of Technology in The Netherlands used LCA to compare three types of architectural coatings: a conventional solvent-based alkyd, a high-solids alkyd, and a water-based acrylic. (Geurink and Bancken, 1992)[6] Although the authors noted that there may be differences in performance or durability among the various coatings, they assumed for purposes of their analysis that the three coatings provided equivalent durability -- i.e., that a new topcoat would be required every five years, and that the surface would need to be stripped and recoated at the end of 20 years.

This paper does not attempt a complete review of the methodology and assumptions of Eindhoven study. The major conclusions of the study were as follows:

- As expected, VOC emissions from waterborne and high-solids coatings were lower than those from the conventional solvent-based coating.

- However, even the difference in VOC emissions was relatively minor when the authors accounted for emissions produced by removal of the coatings at the end of their 20-year useful life. Taking these emissions into account, the VOC emissions from the conventional solvent-based coating were approximately 10% higher than those from the water-based coating.

- In terms of environmental impact, the greatest difference between the three coatings was seen in their contribution to water pollution. Effluents to water during production-use-disposal chain from the water-based coating were more than double the effluents from either the conventional or the high-solids coating.

- The authors concluded that "not all levels of environmental criteria are decreased by the new generation decorative paints. Especially [water-based] acrylics show some disadvantages (exhaustion [of natural resources], water pollution, acidification)." *Id.* at 12.

Whereas the Eindhoven study examined architectural coatings, a second recent study sponsored by BP Chemicals, Ford Motor Company, and PPG Industries evaluated alternative coating technologies for an industrial coating operation. (Hazel, 1994)[7] In these operations, low-VOC coatings are not the only option for reducing VOC emissions; rather, various

forms of VOC abatement technologies such as incineration and absorption may also be used. These options have different degrees of effectiveness (and cost-effectiveness) in controlling VOC emissions, and also have other environmental advantages and disadvantages. LCA is a useful tool for analyzing these various tradeoffs.

This second study used LCA to evaluate the environmental impacts of an automotive coating operation using a waterborne system compared to the same operation using a solvent-based system with an incinerator to control VOC emissions. As the author of the study points out, the three companies that sponsored the study have good credentials for carrying out such an evaluation. Ford currently operates plants using both technologies; PPG makes both kinds of paint; and BP Chemicals manufactures chemicals that go into both types of systems.

In this study, the level of incineration was adjusted to equalize the degree of VOC control between the two options. By taking advantage of sophisticated computer software (Chalmers "LCA Tool"), it was possible to study systems that produce either the same level of VOC emissions from the paint shop itself or the same global VOC emissions, including manufacture and transportation of raw materials and paint. By holding VOC emissions constant, the assessment was better able to compare the other environmental impacts of the two options.

The study then compared a number of upstream and downstream environmental impacts from the two systems, including emissions to air, water, and land and consumption of natural resources. Not surprisingly, the study found that "water-based topcoats have some advantages (principally related to emissions during chemical feedstock manufacture), while solvent-based systems using VOC abatement have others (principally energy related emissions). *Id.* at 8.

For all impacts, the differences were relatively small. The study noted, for example, that "[c]onsumption of gas and crude oil as feedstocks are lower in the water-based system, primarily due to a lower organic content in the basecoat." The authors note, however, that the "amounts involved are small compared to fuel use in the painting process (14%) and insignificant in relation to the consumption [of fuel] by a car." *Id.* at 4.

The fundamental conclusion of the study was as follows:

> Examination of . . . 28 environmental effects (emissions and consumptions) leads to the conclusion that *neither technology has the environmental high ground.* In fact the variability between what is achievable as current good practice within one technology option can be larger than the difference between the base cases considered here.

Id. at 8 (emphasis in original). This conclusion may not be satisfying if one is seeking a single approach for reducing the environmental impacts from coating operations. However,

it serves to illustrate the complexity of addressing environmental issues and the need to evaluate all environmental impacts.

Need to Encourage Advances in All Coating Technologies

Regulations that require product reformulation are often designed to be "technology forcing." In the case of regulations based on low- and no-VOC coating technologies, this means that regulators may expect that future waterborne systems will be able to match the product performance of current solventborne systems. What this approach overlooks, however, is the potential for continuing advances in solventborne systems. When mandated reformulation effectively cuts off further research and development into solventborne systems, it stands in the way of future developments that could offer both performance and environmental advantages.

As noted above, a high-VOC coating that lasts for ten years may be environmentally preferable to a low-VOC coating that lasts for only seven. A technology-forcing regulation may well lead to a lower-VOC coating that lasts for ten years, but it also may cut off further research into solvent systems that would have resulted in a 20-year coating.

Thus, for both economic and environmental reasons, regulatory programs should be designed in a way that allows for advances in all coating technologies, not just in low- and no-VOC coatings.

CONCLUSION

Regulators, environmental advocates, and industry groups should not focus solely on VOC emissions when evaluating the environmental and other impacts of coating technologies. In some cases, reductions in VOC emissions from coating operations offer little or no benefit to the environment and may impose substantial costs on businesses and consumers. Even where VOC emission reductions are needed, the full range of environmental and performance tradeoffs should be weighed carefully. In many cases, traditional solvent-based coatings will continue to be the best option for optimizing total environmental and product performance.

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Life Cycle Analysis of an Aqueous Low V.O.C. Coating

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ABSTRACT:

The accepted method for coating the inside of two piece aluminum cans for beer and beverage is with a water emulsified polymer that contains 15% to 20% of volatile solvents. Development of a water based technology that contains less than 2% volatile solvents has been pursued over the past four years. Coors Brewing Company, Research and Development group, in conjunction with a major manufacturer of polymer coatings, has been developing cooperatively an FDA compliant polymer coating. Testing of this technology in full scale production has been conducted since July of 1994. Once development is complete, this technology should provide a viable low polluting option to the conventional materials even when utilizing end of the pipe control devices. Initial, empirical modeling indicates a 30% reduction in stack and fugitive emissions when compared to a conventional installation utilizing an incinerator. Comparison of this technology with accepted standard waterbased technology reveals a reduction in emissions and/or hazardous waste generation. This reduction is from the point of polymer manufacturer to final disposition of products and wastes. These factors, when combined with operation without the energy utilized in end of pipe control, represent significant pollution prevention gains with resulting benefits of cost savings, energy conservation and the ability to operate in a practical manner.

INTRODUCTION:

The Coors Can Manufacturing Plant, located in Golden, Colorado, is the largest single aluminum can manufacturing plant in the world and produces approximately 4 billion cans a year. The Coors Brewing Company developed the country's first aluminum beverage can, a two-piece aluminum can, in 1959, and was instrumental in the transfer of aluminum can production technology throughout the beverage container industry. The plant currently produces aluminum cans exclusively for the beer beverage market.

Conventional, compliant, aqueous, coating materials used to coat the internal; surfaces of two piece cans for beer and beverage currently contain a relatively high volume of solvent. An alternate technology is under development for coating the internal surfaces of cans that contains a minimal volume of volatiles. The Coors Brewing Company Can Manufacturing Plant has been developing this technology since 1988 and has achieved full production scale test success in July of 1994. The Coors plant is currently the only aluminum can manufacturing plant in the country developing this Ultra Low VOC technology. A technical comparison of can coating technologies is currently in progress.

ALL ESTIMATES ARE BASED ON THEORETICAL CALCULATIONS FROM FORMULATION DATA AND REPRESENT THE POTENTIAL TO EMIT AND ARE NOT MEANT TO REPRESENT ACTUAL EMISSIONS FROM A PLANT.

TECHNOLOGY BACKGROUND:

The can manufacturing industry has been investigating lowering the VOC content of these compliant coatings. Coors also initially investigated lowering VOC content of the coating with the same basic methods employed by most all of the major suppliers. Coors made an early determination that the methods being employed would probably not yield the desired results. A decision was made to investigate the development of a true ZERO VOC material directly. This is in direct contrast to the popular approach of reducing the VOC content in steps. It was determined that with a partner we could pool our finances. We would avoid the costs of the phases involved in the step down approach and apply these moneys directly to the goal of a ZERO VOC material. It was theorized, with high probability, that this goal could be achieved with less expenditure than the stepped approach.

Coors Can Manufacturing has worked in partnerships with several companies with the purpose of developing a coating for the inside of aluminum cans that contains a minimal amount of VOC. The initial push for the investigation of a technology of this type was motivated by a desire to develop a true ZERO VOC coating material. The effects of a technology that was truly ZERO VOC would be to eliminate emissions from the internal coating process, eliminate the requirement for end of pipe controls, reduce potential energy consumption, in addition to a desire to provide greater flexibility for production increases. In 1990, a major coating manufacturer and Coors entered a co-development agreement for the purpose of developing a coating technology that would minimize the volatile components while maintaining the required and desired properties necessary to meet the requirements of beer and beverage packaging.

Currently, the Ultra low VOC coating in use at Coors has sufficient flexibility and withstands post forming and pack stability suitable for the beer beverage market. Newer, more flexible, coatings are currently being developed to meet the broader requirements of the beverage packaging industry.

INTERNAL COATING TECHNOLOGIES:

Potential can coating technologies include the use of conventional solvent based coatings,

aqueous co-solvent coatings, powder coatings, and electrocoat. Among other factors, these techniques differ in the content of solvents in the coatings.

Conventional solvent based coatings contain solvents at concentrations of approximately 80 to 90 percent by volume (1). The solvent composition is typically a mixture of aliphatic hydrocarbons, aromatics, ethers, cellosolves and acetates. As a result, this method produces significant VOC (volatile organic compound) and HAP (hazardous air pollutant) emissions. These coatings have good barrier properties and high quality, but the high VOC emissions have almost eliminated their use for beer and beverage containers.

Aqueous co-solvent coatings contain less solvent than the conventional solvent based coatings (1). In water based coatings, the solids content normally ranges from 15 to 30 percent, the water content from 50 to 70 percent, and the solvent content from 10 to 25 percent. The solvent is used to control viscosity, disperse the solids and as an aid in wetting. Curing is achieved with a thermal oven that requires a high operating temperature due to the high water content in the coating. Since the coating does contain solvents, VOC emissions are still present. This coating method is the most widely used in can manufacturing plants at present time.

Powder coatings are small particles of paint solids that are normally applied to metal by electrostatic deposition, flame spraying or fluidized bed dipping. The solvent content is less than 4 percent, therefore VOC emissions are reduced (1). Normal curing temperatures are also required. This method has not been used in coating beer and beverage cans due to the limitations of coating a small diameter cylinder.

Ultra Low VOC coating application is currently accomplished with standard airless spray equipment. While this was not a development limitation, it provides for the most effortless conversion to this technology as the application equipment does not change. These coating materials are of polymeric origin and crosslink upon exposure to thermal energy. Unlike normal coating polymers that are reacted in solvent media, the main polymer utilized is reacted in water media and amines are added for emulsion stability. This method allows for an extremely low volume of volatiles that are required to be added. This coating technology has been developed and is being tested under full production conditions.

An initial review of feasible technologies and pending air emission regulations indicates that accepted end of the pipe controls or this Ultra Low VOC technology will be the only

technological methods available at this time capable of reducing emissions to the proposed levels.

COATING TECHNOLOGY PROCESS DESCRIPTION:

Aluminum cans are made from large coils of aluminum sheet stock by punching aluminum disks into cups, and sequential drawing and ironing to form the can body. The can body is trimmed, washed and transferred to a printer, where the decorative ink and clear protective overvarnish are applied. The ink and overvarnish are then cured. The cans are then conveyed to the internal coating process. A liquid internal coating is then spray applied to the interior of the can with airless high pressure equipment. The cans are then conveyed to a gas fired continuous mat thermal oven where the coating material is cured. The cans receive further processing where the open ends are reduced in size and flanged to accept the can end after filling and then checked with light for pin holes and other deformities.

In the can coating process (Figure 1), individual stations with high pressure spray equipment are positioned to receive cans to be sprayed. The cans are typically transferred through the spray operation with an indexing star wheel. The star wheel advances each can to the spray position where the can stops momentarily but is rotated positively at high speed (approx. 2,000 rpm). The spray gun is energized and the interior of the can is sprayed with the liquid coating while the can rotates. This rotation allows the complete interior of the can to be coated. The coating material that comprises the dried film must have FDA compliance for this application. The material percentage of solids, normally in the 20% range, and the viscosity are important factors in successful application of a continuous film application.

The cans are discharged from the spray application equipment into or onto a conveying mechanism in route to a thermal curing oven. This mechanism usually provides for an amount of horizontal rotation that assists in maintaining the distributed coverage and prevents pooling or sagging of the applied film. In the thin film wet state the material begins to change and falls out of suspension or emulsion depositing the solid components onto the substrate.

The thermal curing oven is of multi zone design and allows control over the application of heat to the items to be cured. The general concept is to raise the temperature slowly in the first zone. This assists in the release of the solvent present and also pre heats the water for evaporation. The second and subsequent zones are normally heat zones and can

temperatures are raised and held at 400∞F for 30 to 60 seconds. This time at temperature is required to affect the crosslinking of the polymer film deposited and to evaporate the residual water in the coating.

PROCESS EFFICIENCY:

The Coors Can Manufacturing Plant is currently applying both the standard accepted coating material and testing the Ultra low VOC coating material. We are currently evaluating the operational parameters of the new materials in comparison to the normally accepted materials. The Ultra Low VOC material has initially exhibited a greater application latitude that has allowed process efficiency to be at the high end when compared to normal materials.

COST EFFICIENCY:

Cost was not a major concern during the early development stages. The successful development of a material that could be applied, posses the required film properties and contain a minimal volume of VOC was the first and foremost goal. It was recognized by the development team that cost would become a considerable factor to eventual commercialization. Economies of scale in the coating manufacture have not been achieved. Data for the application costs is being collected on a continuing basis. Actual costs can only be estimated at this time. Initial results tend to indicate a definite trend of lower weight of applied film required to achieve the performance necessary. Another initial trend indication is that of improved transfer efficiency or a reduction in loss of material during application.

ENERGY EFFICIENCY:

The total energy consumption requirements have been compared for the Low VOC and the standard technologies with end of pipe controls (Table 1). Estimates in units of millions of BTUs per billion cans are provided. The estimates include both BTU values obtained directly from natural gas (thermal ovens) and BTU values for the electrical power consumption. Since end of pipe controls would not be necessary with the Ultra Low VOC material, approximately 17,405 million BTUs are saved per billion cans or a potential annual industry saving of 1,782,715 million BTUs.

PRODUCT QUALITY:

The quality of the coated interior of the can is an important consideration from both chemical and physical aspects, and as a container for a consumable product. A material must meet the requirements of FDA, laboratory scale application and final film property evaluation as a requisite to being considered for any limited scale use in a production environment. The material currently being tested meets or exceeds the quality requirements established for the physical can profile utilized by Coors. Additional development of the properties of the final film will be required to meet the specifications of other can profiles and individual requirements of other beverage users.

ENVIRONMENTAL IMPACT AND LIFE CYCLE ANALYSIS:

The low VOC internal coating technology offers the opportunity to realize real pollution prevention and real waste reduction. Wastes are not shifted from one media to another nor are wastes shifted from being emitted to being stored. Preliminary mass balance calculations indicate a net reduction in generated pollutants. It is also pertinent to note that the contaminants are not incorporated into products and volume reductions in pollutants are not neutralized by increased toxicity. The development of this process yields a product that reduces pollutants in both emitted and liquid/solid wastes. These savings are realized from the point of coating manufacture through applied use and final disposition. All the following estimates include values from the point of manufacture to the final applied disposition. The real pollution prevention and real waste reductions are accomplished in these ways:

- The low VOC internal coating is manufactured in aqueous media with no solvent required for manufacture. This fact limits the potential for emission and or end of pipe controls with their energy consumption and associated emissions.
- The low VOC internal coating contains less VOCs and hazardous air pollutants than any current commercial thermal-curable coating.
- A potential for an additive reduction in VOCs and hazardous air pollutants through a significant increase in transfer efficiency requiring less material being sprayed.
- A potential for an additive reduction in VOCs and hazardous air pollutants through superior film properties requiring less material applied.
- A major reduction in hazardous wastes generated during manufacture and during application as the low VOC internal coating and the waste are not classified as hazardous.
- The elimination of the incinerator-generated emissions of CO, NO_x, SO_x, and CO_2 at the application site.

An initial estimate was made utilizing ASTM method 24 testing of the thermally cured coating materials. Method 24 is the approved method for determining the volatile content of coatings. Current materials in general use for internal can coating contain 140.8 tons

of available VOC per billion cans, which is substantially equivalent to most compliant internal can coatings available. The Ultra low VOC can coating material, in contrast, contains 40 tons of available VOC per billion cans produced as measured by EPA Method 24. The same coating material when evaluated by actual formulation data yields only 26.6 tons of available VOC per billion cans produced. This is theorized to be attributed to the known shortcomings of EPA Method 24 which are magnified as the actual VOC content becomes lower. When viewed from the respect of volume of VOC purchased in each coating per billion cans produced, the Ultra low VOC material has an advantage of an 80% reduction of available emissions.

In addition to VOC emissions, CO_2 emission estimates were compared for the two technologies. The CO_2 estimates were calculated from EPA conversion factors for natural gas combustion, and also for CO_2 emission factors for electrical power production. The CO_2 estimates for both technologies therefore include the CO_2 emissions which occur at the power plant generating the electrical power used for the controls and blowers in the thermal oven process. When this technology is compared to incineration, the emissions savings of CO_2 per billion cans produced is currently estimated at 987.25 tons.

Current accepted technology and the proposed Ultra Low VOC technologies were compared for waste saving's impact. The first comparison is of the current technology to the proposed technology, both without incineration. The next comparison is of the current technology with incineration and the proposed technology without an incinerator. Table #2 indicates the proposed technology has a potential waste saving of 150.2 tons per billion cans produced when compared to the current technology without incineration. Table #3 compares the current technology with incineration to the proposed technology without incineration and indicates potential waste savings of 1,048.434 tons per billion cans produced. The Ultra Low VOC technology has the potential to provide a waste saving over currently accepted materials and, if accepted as a regulatory alternative to incineration, can provide substantial pollution prevention and energy savings.

A comparison (Table 4) was made for hazardous air pollutants (HAPs). Almost half of the VOC content in the current compliant internal coatings are glycol ethers, which are listed hazardous air pollutants in the new Clean Air Act regulations. Therefore, it is pertinent that with upcoming higher scrutiny and tighter controls for HAPs, a technology with lower HAP emissions will be highly preferred. Estimated HAP emissions from the normal compliant internal coating is calculated to be 63 tons/billion cans, and estimates indicate that the HAP emissions of the Ultra Low VOC technology are approx. 2.3 tons/billion cans. This represents a reduction of 96%.

Many operating can facilities do not currently utilize end of pipe controls. When estimates are evaluated for these facilities, strictly as a pollution prevention technology, they indicate a potential annual emissions savings per billion cans of 36 tons of hazardous waste, 114.2 tons of VOCs, 60.7 tons of HAPs, 987.25 tons of CO_2 and an energy savings of 17,405 million BTUs.

If acceptance of this technology, as a alternative to thermal destruction, would be accepted, the impact could generate an estimated annual emission savings per billion cans when compared to incineration of 36 tons in hazardous waste, 20.568 tons in VOCs, 9.25 tons in HAPs and 987.25 tons in CO_2.

NATIONAL IMPACT:

If the Ultra Low VOC technology was developed for and transferred industry wide, there would be subsequent notable pollution prevention impacts. The can manufacturing industry is large, with approximately 130 billion cans produced each year. The vast majority of these cans are aluminum cans, approximately 103 billion per year (2). Estimates for the impact of this technology on a national basis have been calculated by increasing the rate per billion cans to the national production rate.

If recognized as an alternative and adopted across the board, Ulta Low VOC technology would result in estimated emission savings from can manufacturing of 3,708 tons in hazardous waste, 2118.5 tons of VOCs, 6,252.1 tons of HAPs, and 101,686.75 tons of CO_2. These impacts can be considered even more substantial taking into account the regional clustering of can manufacturing plants in several states. The development of a material that meets the industry requirements and subsequent implementation of this Ultra Low VOC technology could therefore have a significant impact upon a regional pollution prevention basis.

INDUSTRY ACCEPTANCE:

Current Ultra low VOC coatings, being tested at Coors, have sufficient flexibility and withstand post forming and pack stability for the beer beverage market. Newer, more flexible, coatings are currently being developed to meet the broader beverage packaging requirements. When the new materials become available there should be an enthusiasm in the industry to evaluate these coatings. Technically, these materials can be developed to meet the requirements of the industry.

Cost will continue to be a major concern in the competitive environment of the industry but should improve as the market grows and economies of scale develop. It should be apparent that industry can and will strive to develop systems, processes and materials that will eliminate or dramatically improve pollution impacts from manufacturing. A major consideration will most probably continue to be the impact from Federal, State, and Local regulatory requirements. With the ability of technologies, such as this one, to have such a major impact upon energy savings and pollution prevention it would seem highly advantageous for the regulating agencies to develop specific positive incentive programs. These incentives would be applicable to concerns that would convert to or engage in the development of a similar low polluting technology.

The development of a technology such as this can be a lengthy endeavor and industry tends to be short term and bottom line driven. These considerations make for a situation where any definite positive incentive directed toward assisting industry in growing, remaining competitive and continued operations would prove extremely valuable when developing a financial case for a development program and budget. A cooperative approach between industry and government would generate a measurable success for industry, government, and the environment.

SUMMARY:

The Ultra low VOC coating technology being tested at the Coors Can Manufacturing Plant has been a developmental success for about one year. Very substantial pollution prevention benefits are evident with this technology in very low, or zero, VOC and HAP emissions, and much lower CO_2 emissions when compared to end of the pipe control methods. Initial estimates indicate that the Ultra low VOC technology has the potential to be operationally more cost effective than the alternative technology. This technology is currently being evaluated in a full production scale on a limited test basis at the Coors plant. All production with this technology is currently dedicated to a beer beverage market, and container product quality is fully acceptable for this market. A coating material that is more flexible to facilitate post forming is currently desired for many other beverage markets. New generations of coatings designed around this technology will have to be developed for the requirements necessary to be acceptable as a universal beer and beverage material. Now that the technology of producing an Ultra Low VOC can coating has been developed, future formulations should be capable of being brought to market in approximately one-half the time or less. The requirements will have to be investigated and a material developed prior to this technology being considered for use on a national basis.

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TABLE #1
Energy Savings.

Technology	a Current with	b Proposed	(c=a - b) Energy savings
MM/BTU Billion	18,445	1,040	17,405
MM/BTU per Industry Year	1,889,835	107,120	1,782,715

TABLE #2
Waste Savings.
Comparison of both without incineration.

Waste generated	(a) Current technology (tons/billion)	(b) Proposed technology (tons/billion)	(c = a - b) Waste savings (tons/billion)
Hazardous Waste Scrap	36.000	0.000	36,000
VOC	140.800	26.600	114.200
CO	0.013	0.013	0.000
NO_x	0.238	0.238	0.000
SO_x	0.538	0.538	0.000
CO_2	67.000	67.000	0.000
Total of waste (tons/billion)	244.589	94.389	150.200

TABLE #3
Comparison with an incinerator on the current technology;

Waste generated (tons/billion)	(a) Current technology (tons/billion)	(b) Proposed technology (tons/billion)	(c = a - b) Waste savings (tons/billion)
Solid Waste Hazardous	36.000	0.000	36.000
VOC	47.168	26.600	20.568
CO	0.304	0.013	0.291
NO_x	4,313	0.238	4.075
SO_x	0.788	0.538	0.250
CO_2	1,054.250	67.000	987.250
Total of waste (tons/billion)	1,142.823	94.389	1,048.434

TABLE #4
HAZARDOUS AIR POLLUTANTS

Technology	HAPs Tons per Billion	HAPs tons per Industry Year
Current no Incinerator	63.0	6,489.0
Current with Incinerator	9.25	952.75

Proposed Low VOC	**2.3**	**236.9**

SESSION 5

APPLICATION TECHNOLOGIES/SURFACE PREPARATION

PAPERS PRESENTED:

"Advances in Aerospace Coating Technologies: Convergent Spray Technology "
(Paper not available for publication.)
by
Douglas Deason
United Technologies
Huntsville, Alabama

"Encapsulant Lead Paint Remover"
by
Jeffrey Ellermann
Kwick Kleen Industrial Solvents
Vincennes, Indiana

"Utilization of Effervescent Spray Technology to Eliminate Volatile and Toxic Diluents"
by
Michael Smith
Thiokol Corporation
Brigham City, Utah

"SERDP, USMC Spray Booth Control and P2 Demonstration"
by
Charles Darvin
U.S. Environmental Protection Agency,
National Risk Management Research Laboratory
Research Triangle Park, North Carolina

ADVANCES IN AEROSPACE COATING TECHNOLOGIES: CONVERGENT SPRAY TECHNOLOGY

by

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ABSTRACT

Significant gains in the reduction of volatile organic compound (VOC) emissions from industrial painting and finishing operations have been achieved in recent years. However, all classes and types of coatings have not been adequately addressed with best available technology. This is especially true for high thickness protective coatings requiring significant solvent usage to deliver and spray-apply these highly filled coating systems. This paper will present a pollution-preventing technology that uses a solventless spray process to rapidly deposit lightweight highly-filled coatings. This innovative spray process, Convergent Spray Technology®, produces high thickness, high performance coatings while eliminating VOCs, significantly reducing hazardous waste, and using reclaimed or low cost materials as fillers. Convergent spray is so named because the multi-component solvent-free resin system is mixed within the spray gun, is then atomized and this stream is converged with the pneumatically delivered powder (filler) stream at the patented spray gun. Through this method, solvents are no longer required to reduce the viscosity of the mixture because the filler is separate from the liquid part of the materials supply system. USBI, the prime contractor on the Space Shuttle Solid Rocket Booster (SRB) program, is active in broadening the use of the convergent spray process having already demonstrated the capability of this process to replace thermal protection materials that use methylene chloride and perchloroethylene and Freon® for launch vehicle applications.

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Encapsulant Lead Paint Remover

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The purpose of this project is to develop a safe and effective way to remove lead based paint from structures in need of lead abatement. Lead poisoning occurs in thousands of people every year, the majority being children. The sole purpose of lead abatement is to remove the lead hazard. This must be done without creating other hazards. These additional hazards would include production of harmful lead dust and chemical vapors from volatile organic compounds. Removing these hazards can also reduce cost. Less ventilation and filter equipment are needed and a much safer working environment is created for the employee. Until now, the majority of removal processes created lead dust or VOC vapors. With the Encapsulant Lead Paint Remover project, a method of removal has been developed which creates no lead dust and emits little or no VOCs into the environment.

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

The risks of children as well as adults being exposed to lead has been well documented in the past five or six years. Even children with low levels of lead poisoning show decreases in their IQ scores and other health problems.[1,2,3,4] Occupational lead exposure remains one of the oldest and most prolific health hazards for working adults.[5] The major source of lead exposure is from paint chips and paint dust. If lead based paint is in or on a home, it can be loosened in several fashions. Older style homes have windows that slide up and down. Paint that is present where the window moves will be ground into fine dust and the lead will become a part of the living environment. It is possible that whatever children touch may contain lead dust and will be transferred to their mouths, and then, the lead poisoning begins. The paint on the outside of the house may flake off and easily be tracked into the house becoming part of the living environment with the same risk. Similar scenarios can be built for doors, walls, and porches that have lead paint.

The problem of lead poisoning has always been considered greatest in children, however recently there has been concern for those who are working in lead base paint abatement. The Occupational Safety and Health Administration has adopted a final standard for occupational exposures to lead. This standard limits occupational exposure to 50 micrograms per cubic meter based upon an eight hour time weighted average. The basis for this standard is evidence that exposure to lead must be maintained below this level to prevent material health impairment and/or affect the functional capacity of exposed employees.[2] In 1992 the Centers for Disease Control issued an alert that was a "request for Assistance in Preventing Lead Poisoning in Construction Workers."[6] They cited new evidence which associates lead poisoning with abrasive blasting, sanding, cutting, burning or welding of bridges and other steel structures coated with paints containing lead. The following year the National Institute for Occupational Safety and Health created the Adult Blood Lead Epidemiology Surveillance program due to a concern for lead exposure in workers depainting structures such as bridges and water towers.[7]

Many homes still exist that have bottom layers of paint that were prepared by stirring white lead, linseed oil and turpentine together until a smooth mixture was attained. After several days the paint dried, but soon started to flake. Commercial house paints became available and often contained lead. The use of paints containing lead in private residences was banned in 1978. As many as 75 percent of homes built before 1980 are reported to have some lead based paint in them. There are several commercial products on the market that are effective in testing for the presence of lead in paint.[8,9]

There have been several approaches to the removal of lead based paint, each having advantages and disadvantages. Surfaces that are small and can be easily removed from the home or structure can be taken into a shop and stripped using a solvent based stripper. The risk of the organic stripper itself aside, this approach is appealing because it contains the lead very well. The lead is contained in the waste liquid and standard flocculation methods can be used to clean the waste water to levels that are acceptable for disposal. If the worker elects to use a high pressure water wash to remove the paint residue and the organic stripper, there is a high risk that the residue of lead still on the item being stripped will be atomized and enter the breathing zone of the worker. This risk may be greater than acceptable. Other methods of cleaning the remover and

residue from the item are quite safe and effective, but more work intensive. Organic solvent stripper in a semipaste form may be used on surfaces that cannot be taken into a shop. Clean up is difficult and work intensive, but reasonably safe if high pressure wash is avoided. Exposure of the worker to the organic solvents and the release of VOCs to the environment are hazards that must be considered if this approach is used.

Perhaps the most widely used approach to the removal of lead based paint is mechanical. Blasting is often used because it is portable and removes the paint. Containment and collection of the paint chips and the dust is very difficult. The dust generated makes it likely that anyone in the area will breath the lead containing dust. This is evidenced by the concern for the workers mentioned earlier who were stripping and repainting bridges. If the stripping is outside of the house, can the soil be protected from contamination and subsequent "tracking" into the home? If interior surfaces are sand blasted can all of the dust be removed from environmental surfaces? In most cases the answer is "No".

Another approach is to encapsulate the lead paint right where it is. The appeal is that there should be little or no exposure to workers. The fact remains that the lead problem is still present and will have to be faced sometime even if it is not until the structure is razed. An effort has been made to use a water based stripper that removes the paint in clumps and stabilizes its lead content.[10] While this is a good approach, the product is usually in place until it is dry, then when it is removed dust is again generated with all the risks that accompany it. This method of application is very labor intensive and difficult to use for large projects.

Individuals engaging in lead-based paint activities should be properly trained and certified. Training should include proper work practices and health and safety protection. In addition to employee training, engineering and work practice controls which would minimize the level of airborne lead must be implemented. This includes modifying or substituting established processes, equipment or products; equipping exhaust ventilation equipment with a dust collection system to capture lead dust and fumes at the point of generation; and amending general work practices to reduce the spread of dust. Other work practices and engineering controls such as increasing the exhaust ventilation system and keeping the worksite as clean as possible should be developed and, where possible, put into effect.[11] In addition to protecting its own employees, the construction contractor will be expected to conduct its activities in a manner to protect third parties from exposure to hazardous materials. OSHA is drafting guidelines which would limit the chemicals to which office workers may be exposed. The contractor will have to be careful that its activities will not expose those workers to lead dust or chemicals which exceed the OSHA limit.[6] These controls to improve the work and health conditions are costly and time consuming. An abatement method which would eliminate the lead dust or chemical vapors could drastically reduce cost and time. The air filters and ventilation equipment are not necessary if little or no air contaminates are produced.

The alternative seems to combine the advantages of the existing methods and eliminate their collective risks. Whatever the method, it must remove the lead based paint from the substrate. Elements of a good approach would contain the lead based paint in a matrix without the generation of dust. The system needs to be portable enough to be taken to any site and the

stripper easily be applied to large surfaces. Simple flocculation methods to clean up small amounts of wash water can easily be used to reduce waste.

The approach recommended is one that uses a water based stripper that is strongly alkaline. This has been used to remove paint for some time and is very effective. It may darken the wood, so if a clear finish is applied after stripping, a wood toner must be used. Along with the aqueous alkaline solution a polymer that is swelled by the alkaline solution is used. The result is a material that has a high viscosity and a good cohesiveness. When this is applied to the paint, the aqueous alkaline solution softens the paint and the paint film is absorbed into the polymer. This stripper will not work as fast as a methylene chloride solvent stripper, but it will penetrate multiple layers of paint in an hour. The resident time will be dependent upon the number of layers of paint, the temperate and other environmental conditions. When the paint is completely absorbed into the remover matrix, the film can be removed with a putty knife or joint knife. The knife can be used to get under the film, which can then be peeled off in long rubbery strips. The remover that has been in contact with the air will become rubbery and form a substantial film. The film will seal the stripper that is under it and it will stay moist for a longer period of time. Just how long it will stay moist will depend on the temperature and other environmental conditions. The strips that are removed can be collected in a plastic bag, sealed, and disposed of by methods normally used for hazardous waste. The wood remaining will be moist and will have a small amount of residue. This can be gently washed and the small amount of water collected. Trisodium phosphate in the wash water will help to immobilize the lead. The waste water can then be flocculated and the lead concentration will be reduced to levels that are considered acceptable for wastewater. The total mass of the remover applied to the paint is small, and as a part of the curing process, there is evaporation of the water solvent thus the total mass of the stripper is reduced without adding VOCs to the environment.

A thick semipaste form of the stripper can be applied with a putty knife. This is ideal for small areas but would be very work intensive for large walls and structural surfaces. The product in a liquid form can be applied with a wand. The product is designed as a two part system, each is a water like solution that can easily be pumped. It is recommended that air driven pumps be used to deliver each of the solutions to a specially designed wand. The solutions mix about two inches beyond the end of the wand, and react immediately to form a high viscosity material similar to the semipaste. It can be removed in the same manner as the semipaste form after an appropriate curing time.

The white lead paint applied directly to bricks is very difficult to remove, and it will be necessary to remove the layers of more modern coatings, and then apply a second coat of the stripper to the base coat in order to remove it.

The advantages of this form of lead based paint remover are:

1) There is never any lead laden dust generated.
2) The paint is encapsulated in a moist tough film.
3) The remover itself does not add very much mass to the waste stream.
4) The lead in the wastewater from the final cleanup is easily removed and disposed of.

5) Application is easy for either large surfaces or small surfaces.
6) Cost to set up is low.
7) Cost of aqueous strippers is low.
8) Since it is a water based remover there are no VOCs.

Lead poisoning must be reduced. The best way to do this is to eliminate the source of the lead. As stated before this must be done in the safest manner possible to prevent additional cases of lead poisoning from occurring during the abatement process or after the abatement is finished. With dedicated research and new technology, the process described in this paper will enable the abatement of lead paint from substrates without introducing airborne lead dust or VOC vapors into the breathing environment.

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Utilization of Effervescent Spray Technology to Eliminate Volatile and Toxic Diluents

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INTRODUCTION

Thiokol Corporation uses several thermal setting urethane and epoxy slurry formulations in the production of rocket motors and pyrotechnic devices. Some of them are used as liners to bond the propellant or illuminant to the case wall. Liner formulations typically contain solids which act as thixotropic agents, thermal resistance and inert fillers. Application of these liners is accomplished by methods such as spraying or atomizing with centrifugal force (sling lining). The solids loading causes an increase in the viscosity so that a diluent is required in order to spray them. Typically ozone depleting, toxic and/or flammable solvents are utilized. The reduction or elimination of these chemicals is an important focus of this conference.

Two illuminant flares with case diameters of two and five-inches are produced at Thiokol. Because of the case diameter, spraying has proven to be the most effective method of applying this liner. The formulation consists of an epoxy binder filled with inert and thixotropic solids. Undiluted this material has a viscosity which ranges between 300 and 500 poise. Methylene chloride is added to the mixture to thin the material to a sprayable viscosity. Devilbiss spray equipment is used with a tip that produces a 45-degree hollow cone pattern. Several passes are required to obtain a liner thickness of 30-40 mils. Multiple passes allows the methylene chloride to evaporate between coats.

Recently OSHA mandated that the current process was unacceptable because worker exposure to methylene chloride was above the threshold limit value (TLV). Two options were proposed to meet reduce or eliminate exposure:

1) Identify a method of spraying undiluted liner.
2) Protect workers by isolating the process with either worker protective equipment or by changes to the facility.

The program decided on the first option based on comparative cost estimates. The following technologies were considered for evaluation to accomplish this goal:

1) Air assisted
2) Airless
3) Effervescent or two phase flow nozzle

A commercial coatings application company was consulated about the feasibility of using air assisted and airless spray systems. Samples of the undiluted liner were sent for analysis and evaluation. The air assisted system was never evaluated because the viscosity of the undiluted liner was outside equipment parameters.

Airless spray system tests were run and the results were evaluated. Based on these tests, this option was dropped because the pressures required to atomize the liner were too high to spray small diameter tubes. This led to the development and evaluation of the effervescent or two phase flow nozzle.

DISCUSSION

Background

The effervescent nozzle concept was obtained from Purdue University. Work accomplished to date on the University level has focused on characterizing nozzle performance with Newtonian fluids with viscosities up to 100 Cp [1]. The application proposed by Thiokol involved using this technology with viscous non-Newtonian slurries. Purdue University reviewed the rheological properties data of the liner and based on their analysis recommended that Thiokol should proceed with feasibility testing.

Approach

The concept of operation for the effervescent nozzle is shown in Figure 1. It is based on initiating two phase flow under pressure with an aerator chamber which introduces gas into a liquid. This is accomplished upstream from the orifice. As the mixture leaves the nozzle, atomization is achieved as a result of the instability of the gas and liquid phases during rapid depressurization when it expands going through the orifice. This design has been documented by Purdue University in published literature [2]. Theoretical calculations as well as empirical work have shown that atomization is accomplished independent of fluid viscosity. A prototype unit was designed and fabricated for use in spray testing at Thiokol.

The flare program initially drove the search for the effervescent nozzle. When the technology was identified, other programs at Thiokol also expressed interest in conducting feasibility testing. A list of all the materials that were evaluated in this study is given below:

1) Carbon filled epoxy liner (Flare)
2) Asbestos filled polyester liner
3) Carbon filled polyurethane liner
4) Conoco HD-2 preservative grease

Testing was done with the following objectives in mind:

1) Show atomization occurs.
2) Determine drop size, texture and uniformity of sprayed materials.
3) Determine a pressure range for future quantitative evaluations.

Because this was a feasibility study and not meant to characterize the nozzle, only qualitative evaluation of the spraying process and substrates was done. Testing for material and bondline strengths was beyond the scope of this study.

Equipment and Procedure

The spray equipment consisted of the effervescent nozzle connected to liquid and gas manifolds. The liner material was fed to the manifold from a one gallon fluid reservoir. Nitrogen was used to pressurize both the gas and liquid sides. The apparatus used is shown in Figure 2. It is the same design that has been used in documented studies done at Purdue University [2].

The liner was mixed in a Ross mixer using standard Thiokol mix procedures. The end-of-mix Brookfield viscosity was taken at the spray temperature using a TD spindle. Samples were sprayed over the given pressure range holding both the substrate and nozzle stationary. The spray action time was recorded to give an indication of the onset of slumping. Liner thickness was measured using a wet film

gauge. A qualitative determination of the texture and coverage was made by a visual examination. High speed motion pictures as well as real time videos of the spraying process were made. Sprayed samples were then placed in an oven for curing. Still photographs were taken of all the cured substrates.

Results

The results from these feasibility tests are summarized in the sections below. Each one is identified by the sprayed material. The parameters used for spraying are given as well as the results.

Carbon Filled Epoxy Liner (Flare).

The liner was mixed at 75°F and heated to 150°F for spraying. The Brookfield viscosity at 150°F was 400 poise. Atomization pressure ranged between 300 and 500 psig.

Based on these test results it was concluded that the nozzle was able to atomize and spray the above formulation. The material was sprayed in a cone shaped pattern resulting in a filled circle on the substrate. The thickness was uniform across two thirds of the circle but thinned with increasing radius. The surface texture of the sprayed liner ranged from orange peel to smooth at a thickness of 30-40 mils. The best results were obtained when spraying at 500 psi.

In order to spray the flare tubes a hollow cone spray pattern is required. With the success of the feasibility testing, the next challenge was to tailor the spray pattern. First attempts were made with commercial spray tips used in conjunction with the effervescent nozzle. They proved ineffective. A nozzle tip was then designed and tested by Thiokol which was successful in spraying the desired pattern.

Asbestos Filled Poly Ester Liner.

The liner was mixed at 150°F and then sprayed. The Brookfield viscosity at 150°F was 850 poise. Two runs were made at 900 psig using this material. Further testing was suspended because the nozzle clogged.

Based on test results it was concluded that the nozzle was able to atomize and spray the above formulation. The material was sprayed in a cone shaped pattern. However the nozzle clogged before a layer of material could be sprayed. A lumpy non-uniform coat was obtained which was attributed to the fibrous nature of the asbestos.

Carbon Filled Polyurethane liner.

Two batches of liner with this formulation were sprayed. The first batch of liner was mixed at 150°F and then sprayed. The Brookfield viscosity at 150°F was 650 poise. The pressure ranged between 400 and 800 psig.

Based on test results it was concluded that the nozzle was able to atomize and spray the above formulation. The material was sprayed in a cone pattern resulting in a filled circle on the substrate. The thickness was uniform across two thirds of the circle but thinned with increasing radius. The texture ranged from smooth to orange peel at a thickness of 35-50 mils. The best results were obtained when spraying at 750 psi.

The second batch of liner was mixed and sprayed at 75°F. The Brookfield viscosity at 75°F was 1750 poise. Atomization pressure ranged between 700 and 1200 psig.

Based on test results it was concluded that the nozzle was able to atomize and spray the above formulation. The material was sprayed in a cone pattern resulting in a filled circle on the substrate. The thickness was uniform across two thirds of the circle but thinned with increasing radius. The texture of most samples was orange peel at a thickness of 20-40 mils. The best results were obtained when spraying at 900 psi.

CONOCO HD-2 preservative grease.

The grease was sprayed at 75°F (ambient) and 150°F onto a plastic surface to determine coverage and texture. The Brookfield viscosities at 75°F and 150°F were 1400 and 600 poise respectively. The material was sprayed in a cone pattern resulting in a filled circle on the substrate. The material texture was semi-smooth with a thickness of 10-20 mils. This material was atomized well at ambient temperatures at pressures less than 100 psig.

Based on the results of these tests it was concluded that the nozzle was able atomize and spray the above materials. Heating was not required to reduce the viscosity for atomization.

Table I given below is a tabulation of the important data generated in this study.

TABLE I

Material	Viscosity (Poise)	Spray Temperature (°F)	Optimum Spray Pressure (psig)	Thickness (mils)	Texture
Carbon Filled Epoxy	400	150	500	30-40	Orange Peel/ Smooth
Asbestos Filled Polyester	850	150	900	NA	Lumpy
Carbon Filled Polyurethane	650	150	750	35-50	Smooth/ Orange Peel/ Lumpy
	1750	75	900	20-40	Orange Peel
Conoco HD-2 grease	1400	75	< 100	10-20	Semi-Smooth

Summary

In summary, the following observations were made based on the results of feasibility testing. The effervescent nozzle was capable of atomizing all the materials evaluated in this study. Based on visual observations it was seen that the drop size distribution varied greatly within a sample run. All samples were successfully sprayed at pressures less than 1000 psig.

The first priority of this testing was to find a system that would spray undiluted flare liner. The testing outlined above proved the feasibility of using the effervescent nozzle for that purpose. Further evaluations were done with flare liner to characterize the specific spray process. The requirement to

spray a hollow cone were also met with the design of a spray tip used in conjunction with the effervescent nozzle. The flare program is currently in the process of incorporating this technology into the production line.

CONCLUSIONS

Based on the results of these tests, it was concluded that effervescent nozzle is a viable option for spraying high viscosity liquids and slurries at pressures less than 1000 psig. This allowed for the spraying of viscous materials without the use of ozone depleting, toxic and/or flammable solvents as diluents.

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2. Geckler, S.C. and Sojka, P.E., Effervescent Atomization: Limitations due to Viscoelasticity. Thermal Sciences and Propulsion Center School of Mechanical Engineering Purdue University, West Lafayette, IN 47907-1003. In: ILASS-AMERICAS 94, 7th Annual Conference on Liquid Atomization and Spray Systems Extended Abstracts. Bellevue, Washington. p. 181

Utilization of Effervescent Spray Technology to Eliminate Volatile and Toxic Diluents

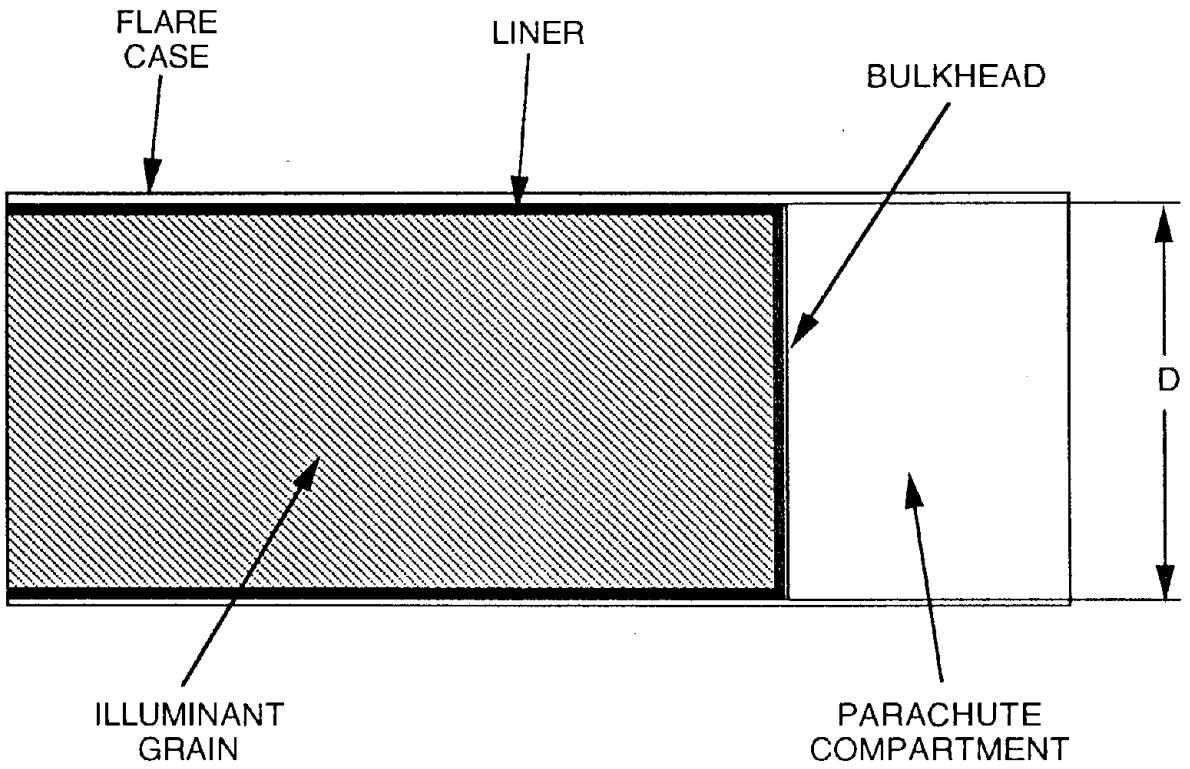
Michael W. Smith

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Thiokol CORPORATION
SCIENCE & ENGINEERING
Adhesive Materials & Processes

INTRODUCTION

- SOME PROCESSES AT THIOKOL REQUIRE SPRAYING OF URETHANE AND EPOXY SLURRY FORMULATIONS
- ILLUMINANT FLARE LINER
  - CARBON FILLED EPOXY
  - 400-700 POISE VISCOSITY @ 75-135°F
  - DILUTED WITH 1:1 RATIO OF METHYLENE CHLORIDE
- WORKER EXPOSURE ABOVE TLV MANDATED ELIMINATION OF METHYLENE CHLORIDE
- SPRAYING UNDILUTED LINER CHOSEN TO MEET MANDATE



D - INSIDE DIAMETER TWO SIZES PRODUCED 2.5- AND 4-INCH CASES

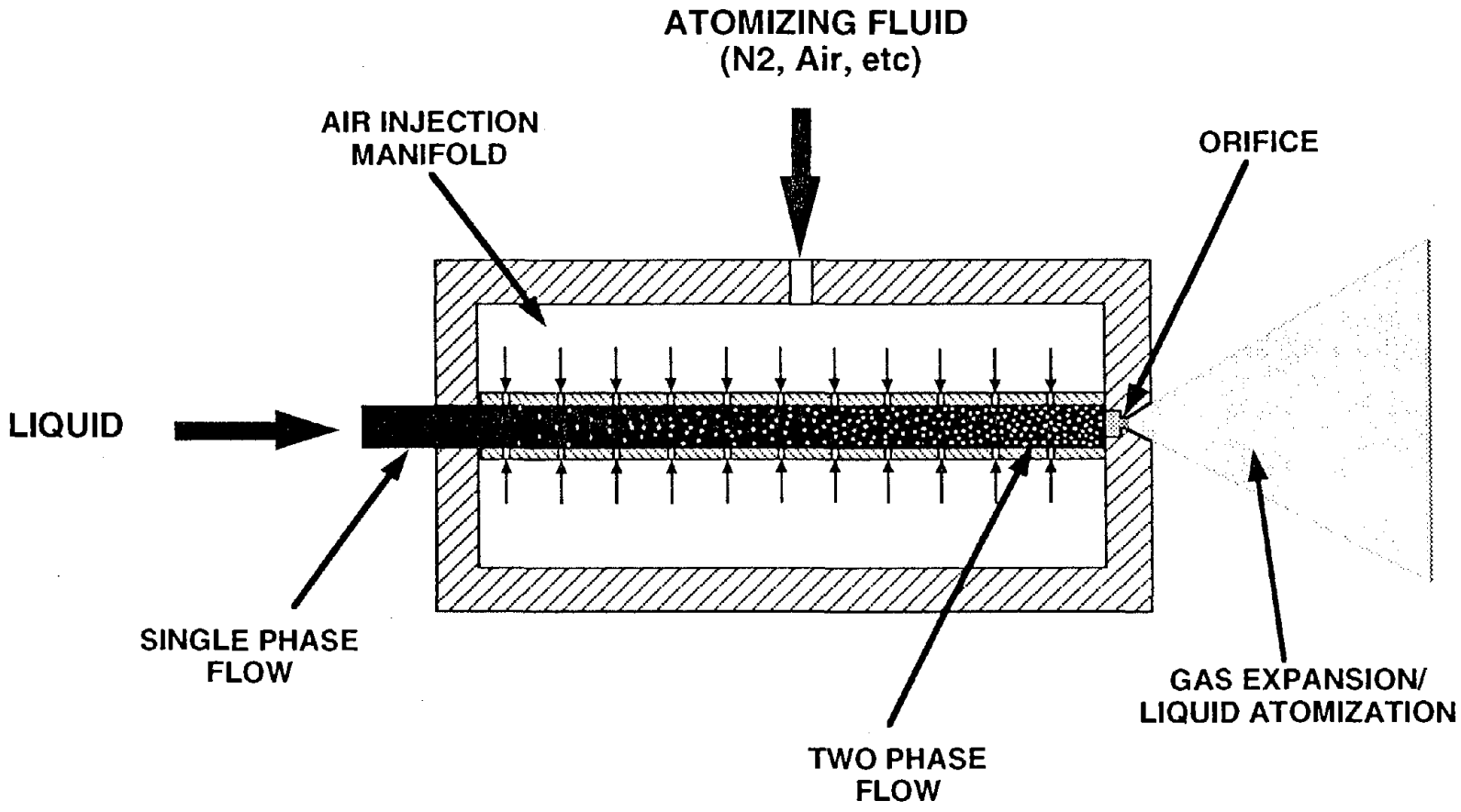
ILLUMINANT FLARE CROSS SECTION

METHYLENE CHLORIDE ELIMINATION

- SPRAYING OPTIONS IDENTIFIED
  - AIR ASSIST
  - AIRLESS
  - EFFERVESCENT NOZZLE
  - CENTIRIFUGAL DISK
- PRELIMINARY EVALUATION RESULTS
  - VISCOSITY OF LINER MATERIAL OUTSIDE OF AIR ASSIST EQUIPMENT PARAMETERS
  - AIRLESS ATOMIZATION OPERATING PRESSURE > 3000 PSIG
    - SAFETY AND PROCESSING CONCERNS
  - EFFERVESCENT NOZZLE CHOSEN FOR FURTHER EVALUATION
  - CENTRIFUGAL DISK COULD BE USED AS A BACK UP IF REQUIRED
    - UNABLE TO LINE SMALL DIAMETER CASES

EFFERVESCENT NOZZLE EVALUATION

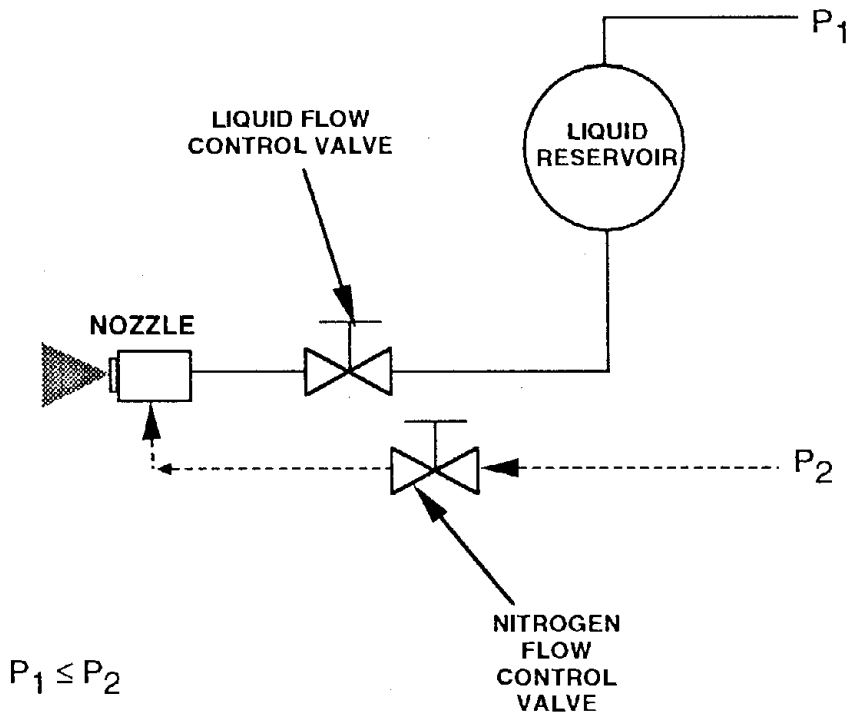
- BACKGROUND
  - CONCEPT OBTAINED FROM PURDUE UNIVERSITY
  - PROVEN WITH NEWTONIAN FLUIDS WITH VISCOSITIES UP TO 100 cP
  - THIOKOL APPLICATION FOR NON-NEWTONIAN FLUIDS WITH VISCOSITIES RANGING BETWEEN 500-2000 POISE



EFFERVESCENT NOZZLE CONCEPT DRAWING

TESTING

- MATERIALS EVALUATED AT THIOKOL
  - CARBON FILLED EPOXY (FLARE LINER)
  - ASBESTOS FILLED POLYESTER LINER
  - CARBON FILLED POLYURETHANE LINER
  - CONOCO® HD-2 PRESERVATIVE GREASE
- OBJECTIVES
  - SHOW ATOMIZATION OCCURS
  - DETERMINE
    - TEXTURE AND UNIFORMITY OF SPRAYED MATERIAL
    - PRESSURE REQUIREMENTS
  - FLARE LINER SPRAY PATTERN
    - HOLLOW CONE



LIQUID LINE	———
NITROGEN LINE	- - - - - - - -

SPRAY EQUIPMENT SCHEMATIC

PROCESSING

- LINER MATERIALS MIXED IN ROSS MIXER USING STANDARD THIOKOL PROCEDURES
- END-OF-MIX (EOM) BROOK FIELD VISCOSITY AT MIX TEMPERATURE
  - TD SPINDLE @ 5 RPM
- SUBSTRATE AND NOZZLE HELD STATIONARY DURING TESTING
  - KRAFT PAPER USED FOR SUBSTRATE
  - FILLED CONE SPRAY PATTERN
- LINER THICKNESS MEASURED WITH WET FILM THICKNESS GAUGE

RESULTS

- OBJECTIVES MET FOR SPRAYING FLARE LINER @ 75°F
  - VISCOSITY - 600 POISE
  - SPRAY PRESSURE - 500 PSIG
  - SPRAYED HOLLOW CONE SPRAY PATTERN
- OTHER MATERIALS

Material	EOM Viscosity (Poise)	Spray Temperature (°F)	Optimum Spray Pressure (psig)	Thickness (mils)	Texture
Asbestos Filled Polyester	850	150	900	NA	Lumpy
Carbon Filled Polyurethane	650	150	750	35-50	Orange Peel
	1750	75	900	20-40	Orange Peel
Conoco HD-2 grease	1400	75	<100	10-20	Semi-Smooth

SUMMARY

- NOZZLE PROVEN FEASIBLE IN SPRAYING A NUMBER OF THIOKOL MATERIALS
- ALL SPRAYING ACCOMPLISHED AT LESS THAN 1000 PSIG
- FILLED CONE AND HOLLOW CONE SPRAY PATTERNS ACHIEVED
- FLARE PROGRAM CURRENTLY IMPLEMENTING EFFERVESCENT NOZZLE IN LINER SPRAY PROCESS

CONCLUSIONS

- EFFERVESCENT NOZZLE IS CAPABLE OF SPRAYING NON- NEWTONIAN FLUIDS
- CAN BE USED TO ELIMINATE HAZARDOUS DILUENTS
  - VOC
  - ODC
  - TOXIC
  - FLAMMABLE

SERDP, USMC

SPRAY BOOTH CONTROL AND P2 DEMONSTRATION

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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Office of Research and Development
Washington, DC 20460

INTRODUCTION

In 1993, the Strategic Environmental Research and Development Program (SERDP) office approved a research program to provide a comprehensive pollution prevention (P2) strategy for military depot facilities. The research and development (R&D) is being conducted by a consortium consisting of the U.S. Marine Corps (USMC), Pennsylvania State University's Applied Research Laboratory (ARL), and the U.S. Environmental Protection Agency (EPA).

The goal of this research program is to develop and evaluate innovative manufacturing and emission control technologies that manifest a P2 philosophy to reduce total emissions from manufacturing and maintenance processes. The focus of the program is on painting and surface cleaning operations which represent over 75 percent of the total pollutant emissions from typical Department of Defense (DoD) facilities.

The program is divided into two parts. First, innovative P2 technologies for painting and surface cleaning processes will be identified. Full scale demonstration of acceptable alternatives will follow. Anticipated technologies to be studied and demonstrated include ultra low volume (ULV) paint technology, which is predicted to reduce paint use and emissions by 25 percent; and the use of n-methylpyrrolidone (NMP), as a surface cleaning solvent substitute alternative for methylene chloride.

Second, R&D studies will be conducted on the use of ultraviolet/ozone (UV/ozone) radiation destruction of volatile organic compound (VOC) emissions integrated into a novel spray booth flow management design concept. Fundamental and applied research on the UV/ozone technology will be conducted at the ARL, utilizing a 2000 cfm (56.6 m^3/min) pilot scale laboratory system. The results will be transferred to and implemented in a full scale 45,000 cfm (1274 m^3/min) demonstration system. An integral part of this demonstration is the full scale validation of the exhaust flow management concept called recirculation and partitioning. This concept will reduce the control system treatment volume from 120,000 to 45,000 cfm (3398 to 1274 m^3/min). This booth design concept will significantly reduce the cost of operating emission control technologies for paint spray booths.

PAINTING AND SURFACE CLEANING PROCESSES

ULV Paint Delivery System

An initial objective of the evaluation of an innovative paint pumping device (the ULV system) was to prove its feasibility for the Marine Corps Logistics Base (MCLB) Chemical Agent Resistant Coating (CARC). The ULV system tested, manufactured by Air Compliance Technology, Greensboro, GA, is a paint delivery system designed to improve the performance of airless guns. It is different from conventional high-pressure paint systems in that, rather than using a piston pump to pump the paint to high pressure, it uses a nitrogen-pressurized floating piston to pressurize paint in a high-pressure-capacity container. Improved performance is obtained primarily because the ULV system allows airless spraying at a lower paint pressure than conventional airless (500-800 psi [3447-5516 kPa] for ULV vs. 1500-2000 psi [10,342-13,790 kPA] for conventional airless).

During preliminary trials by the manufacturer, it was found inappropriate for this type of application. Higher pressures (700-800 psi) caused compaction of the material in the lines and on strainer and filter screens. This clogging effect can be eliminated if pressures lower than 500 psi are used. The materials sprayed with the ULV system included one- and two-component CARCs and a primer. The spray pattern was found unacceptable, having heavy "crows feet" or heavy edges.

N-methylpyrrolidone (NMP)

The objective of this task was to demonstrate the effectiveness of P2 technologies or processes in reducing hazardous air pollutant (HAP) emissions resulting from paint stripping by immersion in methylene chloride. Methylene chloride is a HAP, a suspected carcinogen, and one of 17 chemicals on the EPA's 33/50 list of priority pollutants. NMP, a non-HAP and less volatile solvent, was identified and tested as a paint stripping alternative to methylene chloride and is currently being used at the MCLB in Albany, GA.

FLOW MANAGEMENT AND CONTROL TECHNOLOGY

Air Recirculation and Partitioning

The dominant factor in controlling spray booth emissions is the cost resulting from the need to process large volumes of contaminated air. Therefore, the main objective of this task was to reduce the amount of contaminated air to be treated by an end-of-pipe control technology while maintaining safe working conditions. This objective was achieved by modifying a spray booth using the recirculation and exhaust flow partitioning concepts.

Recirculation reduces the flowrate volume to the booth that would be discharged to an end-of-pipe control system on a spray booth. The technique recirculates a portion of the exhaust air back to the spray booth thus decreasing the flow volume passing to the atmosphere which requires treatment. During recirculation, a portion of the exhaust stream must be removed from the recirculating stream and vented to a control device. Before reentering the booth, the recirculated air is mixed with fresh air equal in volume to the exhaust air and sufficient to guarantee that the booth atmosphere remains at an acceptable level to ensure fire and worker safety. Coupled with recirculation is the benefit caused by a concentration gradient formed in the booth during painting. Tests of this concentration gradient revealed that higher average vertical concentration tended to be segregated in the lower level of the booth downstream from the painting operation. This results in VOC-lean and -rich zones in the booth. Exhaust from the rich zone can be directed to a control device, and the lean zone atmosphere can be recirculated to the booth carrying only a fraction of the generated pollutant.

SESSION 6

POWDER COATINGS

PAPERS PRESENTED:

"Overview of Powder Coatings Technology"
by
Kaye Whitfield
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, North Carolina

"Powder Coatings: Technology of the Future, Here Today"
by
Gregory Bocchi
Powder Coatings Institute
Alexandria, Virginia

"Chlorinated-Maleinized Guayule Rubber in Powder Coatings:
No VOC Thermosetting Chlorinated Rubber Coatings"
by
Thomas Schuman
University of Southern Mississippi
Hattiesburg, Mississippi

"Novel Acrylic Cure Polyester Powder Coating Resin Technology"
by
Eric Dumain
Reichhold Chemicals, Inc.
Research Triangle Park, North Carolina

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Overview of Powder Coatings Technology and EPA's Powder Coatings Research

by

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Presented at the Low-/No- VOC Coating Technologies 2nd Biennial International Conference
Durham, NC
March 14, 1995

The purpose of this paper is to provide a brief overview of powder coatings technology and then to highlight the powder coating research currently in progress in U.S. Environmental Protection Agency's (EPA) Organics Control Branch (OCB).

Introduction and Background

Powder coating is an organic finishing technology that offers users the potential to reduce volatile organic compound (VOC) emissions near zero. Due to ever-increasing VOC emission restrictions placed on manufacturers, powder coatings production and use has been growing dramatically over the past few years at an estimated rate of 15%.[1] The technology has been accepted by such manufacturing communities as automotive, appliance, furniture, and equipment. However, small business manufacturers have difficulty investigating innovative technologies such as powder coatings due to size and budget restrictions.

Powder coatings are of interest to EPA and industry because of what is generally referred to as the five Es:[2,3,4]

Environmental benefits

The well known environmental benefits are that powder coatings emit very little to no VOCs and hazardous air pollutants (HAPs). These coatings also are compliant with federal government regulations for waste disposal.

Energy savings/conservation

Powder coating systems consume, on average, 50% less energy than conventional systems.

Efficiency

Less application of powder, typically one coat, is required for an acceptable finish as compared to conventional solvent-borne coatings; therefore, powder coating is more efficient. Since rejection rates per part are usually lower, an increase in production occurs, which also increases efficiency.

Economic benefits

According to representatives at Reichold Chemical Company's Coatings Division,[3] businesses that convert to powder technology usually experience a payback period of 1 year or less.

Excellence of finish

The finish on substrates coated with powder is excellent, and the appearance of the end product is greatly improved, especially when compared to solvent-borne coatings.

Current EPA Research in Powder Coatings

The strategic focus of EPA's OCB is VOC/HAP elimination and reduction; therefore, powder coatings technology is a logical area to focus our research efforts. One of the greatest advantages of powder coatings technology is that it is environmentally acceptable because of its potential to replace HAP and VOC emitting solvent-borne coatings. Some other advantages of powder coatings are that they are :[2,4]

- 100% solids;
- recyclable (the over spray from the powders is 99% reusable);
- durable and exhibit superior quality in appearance and protection;
- simple to use;
- relatively safe; and,
- environmentally acceptable.

Some of the disadvantages of powder coatings technology are that they are:[2,4]

- restricted to mostly metal substrates;
- not flexible (color changes are limitations); and
- difficult to coat if the part is a complex geometry.

EPA and the National Defense Center for Environmental Excellence (NDCEE), with funding

from EPA's Environmental Technology Initiative, are conducting a study to demonstrate the applicability of powder coatings technology for small businesses. The objectives are to 1) gain a more widespread use of powder coating application technology in order for small businesses to have an alternative to conventional solvent-borne coating use, 2) demonstrate the viability of these systems, and 3) provide an economic analysis as an incentive for small businesses to convert.

Summary

Powder coatings technology has the potential to reduce and/or eliminate many sources of HAPs and VOCs. For that reason, EPA has chosen to focus research efforts on helping a group that, in aggregate, is a major emitter of VOCs and HAPs, small businesses. Since small businesses may not have the resources to explore alternative technologies, this study will allow for conversion to a more environmentally acceptable technology without making any financial expenditures.

Although a demonstration of powder technology has been conducted for EPA, the data from the study are in review; therefore, no results are available. However, initial findings show that powder coatings technology may be a viable alternative for small businesses, and that the technology may prove economical as well.

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POWDER COATINGS:
Technology of the Future, Here Today

An Overview of Powder Coating Materials, Equipment and Applications

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

POWDER COATINGS:
Technology of the Future, Here Today

1.0 INTRODUCTION

This report provides an overview on the current status of powder coating technology in 1993. The use of powder coating in North America is increasing at a remarkable rate of 12 percent per year in pounds of powder sold;[1] a consequence of recent improvements in the technology to manufacture and apply powder coatings, coupled with environmental considerations. There are currently about 3,000 powder coating operations in the United States and the number is increasing rapidly.[2]

From an environmental standpoint, the increased use of powder coatings as an alternative to liquid, solvent-based coatings results in significantly less emissions of volatile organic compounds (VOC's) and hazardous air pollutants (HAP's) as defined by Section 112 of the Clean Air Act Amendments of 1990. (Most of the HAP's released by the coatings industry are solvents that are volatile organic compounds although other air toxics may also be a constituent of some coatings.) Furthermore, powder processes can also reduce energy consumption and hazardous waste generation. Because powder coatings are applied as dry, finely divided particles, no VOC's are released during application and only minute quantities are released during the curing process. Further, in contrast to most liquid painting processes, powder overspray can be recovered and reused, rather than discarded as waste or hazardous waste. Use of powder coatings is seen by many air and other pollution control agencies as a means of reducing VOC's, HAP emissions, and hazardous waste from industrial finishing operations.

This report provides technical information on powder coatings as well as examples of the types of commercial products being powder coated. It is anticipated that this will assist state and local agencies evaluate the relationship between powder and air pollution control and hazardous waste reduction technology by answering questions concerning performance, applicability, costs, and availability.

The information presented in this report is based on data obtained from literature searches, contacts with several state and local air pollution control agencies, written survey questionnaires, and industry experts.

The remainder of this report is divided into six sections. The first section provides a brief history of powder coatings from the 1950's into the 1990's. The next describes the different classes of powder coatings that are currently available, including those very recently developed. The types of equipment required for a powder coating line are described in Section 4. The types of products that are typically powder coated are listed in Section 5. Section 6 discusses the economic advantages of using powder coatings and presents a cost comparison between powder and liquid coatings. Section 7 presents conclusions drawn from the study and Section 8 provides a list of references for the reader who wishes to explore the subject in greater detail.

2.0 BACKGROUND

The technology for finishing metal products with dry powder coatings rather than with conventional liquid paints has been available in this country since the mid-1950's. By the late '50's, powder was being used to coat pipe for corrosion protection and electric motor parts for insulation. These early powder coatings were applied using a fluidized bed process in which heated parts were dipped into a vat where the powder is fluidized by air. The particles of powder that contact the heated metal parts would adhere and soften and flow into a smooth even layer. Most coatings applied in these fluidized beds were vinyl or epoxy powders. Typical coating thicknesses ranged from 150 to 1,000 μm (6 to 40 mils) and the applied coatings were functional (e.g. for corrosion resistance) rather than decorative.[3]

During the evolution of powder coating technology, several disadvantages or potential problems were identified. Most have since been resolved or minimized. The following are some of the problematic issues of the past:

1. Any process that required frequent color changes would entail extensive downtime. The ability to apply a wide range of colors was restricted by equipment limitations and changeover times. Rapid color changes typically required multiple booths, with each booth dedicated to specific colors. Also, special equipment was required to isolate and recover different colors in order to gain the economic advantages of recycling the powder.
2. Storage and handling of powder was sensitive to temperature and humidity; powder would not fluidize well if exposed to excessive moisture.
3. Accurate feeding of powder to the spray gun was often difficult. The result was uneven flow and variations in film thickness.
4. Color matching and color uniformity was potentially more difficult to achieve than with liquid coatings.
5. Uniformity of coating thickness was sometimes difficult to maintain and thin films 25 to 51 μm (1 to 2 mils) were sometimes difficult to achieve.
6. Cure temperatures required for some powders were so high that their use would risk damage to solder joints or temperature-sensitive parts of items being coated.
7. Powder coatings were especially susceptible to "Faraday cage" effects which prevented charged particles from adhering to internal corners and recessed areas.
8. Airflow in the booth and the area prior to the oven had to be carefully controlled to avoid dislodging spray-applied powder that is held in place primarily through electrostatic attraction.
9. Because of the extra equipment requirements (multiple booths, powder handling, application and recovery systems), conversion of an existing liquid line to powder was often expensive.

Technological advances that have addressed and minimized or eliminated most of these issues are discussed in this report.

The primary development that opened the way for powder coatings to become a major factor in the metal finishing industry was the introduction of the electrostatic spray process in the early 1960's. Electrostatic spraying allowed 1) the application of relatively thin layers of powder coatings and 2) powder to be used on parts that could not be heated or dipped in a fluidized bed. Powder coatings, for the first time, became an economically viable alternative for decorative as well as functional coatings.

The emergence of powder coatings as an alternative to liquid decorative coatings led to the development of a variety of resin systems specifically designed to meet the needs of the diverse user industries. Epoxy resins were used almost exclusively during the early years of powder coatings. Polyesters, polyester/urethanes, epoxy-polyester hybrids, acrylics, and polyvinylidene fluoride have now become equally accepted resin systems, each having its own market share depending on the performance characteristics needed for the product. Powder coatings are currently available in clear and virtually any color, gloss level, or texture.

Recent advances in application technology also have allowed powder coatings to be used by an increasing number of industries. Automated finishing systems that allow rapid and frequent color changes and high powder utilization efficiencies resulting in minimal waste have made powder an economical coating in many high-volume industries. (Powder utilization is a term used to reflect the waste per unit of coating sprayed. It credits overspray that is captured and recycled when expressing efficiency as the percentage of total powder sprayed that is deposited on the work piece.)

3.0 POWDER COATING MATERIALS

As recently as the early 1970's, the powder coating industry had a limited number of solid resin systems on which to base powder formulations. Consequently, the ability of the powder coating industry to meet the diverse needs of the finishing industry was also limited. For several reasons, including increased concerns over VOC emissions, worker safety, and energy costs during the 1970's, the popularity of powder coatings grew until powder coatings represented almost 11 percent of all industrial coatings used in the finishing industry by 1992.[4] As interest in powder coatings has continued to grow, the industry has simultaneously responded with technological improvements. These include:

1. New, more efficient application and recovery equipment.
2. The ability to match virtually any color or texture with powder coatings. While there have been limitations in producing certain metallic effects with powder coatings, technology is continuing to perfect the metallic look.
3. Improved powder resin systems that provide a wide range of properties including performance, gloss, film thickness, and texture, that can coat not only metal, but also glass and ceramics.
4. The addition of infrared curing equipment to replace or supplement conventional gas, oil, and electric convection ovens.
5. The availability of powder in virtually any quantity, to suit the needs of every customer. (Minimum orders vary with the powder manufacturer.)

3.1 THERMOPLASTIC POWDERS

A thermoplastic powder coating is one that melts and flows when heat is applied, but continues to have the same chemical composition once it cools and solidifies. Thermoplastic powders are based on high molecular weight polymers that exhibit excellent chemical resistance, toughness, and flexibility. These resins tend to be difficult to grind to the consistent fine particles needed for spray application, and when heated, have a high viscosity. Consequently, they are applied mainly by the fluidized bed application technique, and used mostly in thick film applications.

Typical thermoplastic powder coatings include: polyethylene, polypropylene, nylon, polyvinyl chloride, thermoplastic polyamides, and thermoplastic polyesters.

Polyethylene powders were the first thermoplastic powder coatings to be offered. They provide excellent chemical resistance and outstanding electrical insulation properties. Polyethylene coatings are smooth, have a medium gloss, and good release properties that allow sticky materials to be cleaned from their surfaces, and are often used as coatings for laboratory equipment.

Polypropylene produces a surface that is very inert and is often used in applications where the powder coated part may be exposed to chemicals. Nylon offers excellent abrasion, wear and impact resistance, and a low coefficient of friction. They are commonly used as mechanical coatings for sliding and rotating bearing applications in appliances, farm equipment, and textile machinery. Polyvinyl chloride provides good durability as well as flexibility. An example of a product coated with polyvinyl chloride is dishwasher racks. Thermoplastic polyamides provide excellent resistance to detergents, impact, and high temperatures. Thermoplastic polyesters offer good exterior durability and weatherability, and do not usually require a primer for good adhesion to most metals. They are often used on outdoor metal furniture.

Thermoplastic powders are especially well suited for a thick coating capable of extreme performance requirements. Because of the inherent thickness of these coatings, they do not generally compete in the same market as liquid paints.

3.2 THERMOSETTING POWDERS

Thermosetting powder coatings are based on lower molecular weight solid resins. These powders also melt when exposed to heat. After they flow into a uniform thin layer, however, they chemically cross-link within themselves or with other reactive components to form a reaction product of much higher molecular weight. The final coating has a much different chemical structure than the basic resin. These newly formed materials are heat stable and, unlike the thermoplastic products after curing, will not soften back to the liquid phase when heated. Resins used in thermosetting powders can be ground into very fine particles necessary for spray application and thin, paint-like coatings. Because these systems produce a finish that offers properties comparable to liquid coatings, most of the technological advancements in recent years have been with thermosetting powders.

Thermosetting powders are derived from three generic types of resins: epoxy, polyester, and acrylic. From these three basic resin types, five coating systems are derived. Epoxy resin-based systems are the most common and are available in a wide range of formulations. They are used for both functional and decorative coatings. Their functional properties include outstanding corrosion resistance and electrical insulation. Decorative epoxies offer attractive finishes that are flexible, tough, have excellent corrosion resistance, and high impact strength. Epoxies lack ultraviolet resistance and therefore, are not recommended for outdoor use because in prolonged sunlight exposure, they tend to chalk and discolor. Various types of hardeners are used with epoxy powder to optimize appearance and properties for use in a wide range of applications. Recent developments allow epoxies to be cured at temperatures as low as 121°C (250°F) for 20 to 30 minutes, or even shorter times at higher temperatures.[5]

Epoxy-polyester hybrid coatings are used mainly for decorative applications. They are more resistant to chalking and over-bake yellowing than pure epoxies but have a lower surface hardness and are less resistant to solvents. Hybrids also exhibit better transfer efficiency and a greater degree of penetration into recessed areas of a part.

Polyester-TGIC coatings contain a polyester resin cross-linked with triglycidyl isocyanurate (TGIC) as a curing agent. These powders offer very good mechanical properties, impact strength, and weather resistance. They are resistant to chalking and are often used for such outdoor applications as patio furniture, lawn mowers, and aluminum extrusions and panels for large commercial buildings.

Acrylic-urethane coatings are formulated with acrylic resins cross-linked with blocked isocyanates. They have excellent color, gloss, hardness, weatherability, and chemical resistance. They have an excellent thin film appearance but are less flexible than polyesters.

Polyester-urethane coatings are formulated with polyester hydroxyl resin combined with blocked isocyanate hardeners. Polyurethane powders exhibit outstanding thin film appearance and toughness as well as good weathering properties.

Table 1 provides a summary of the key physical properties of these thermosetting powder coatings.

3.3 NEWLY DEVELOPED POWDERS

Advancements in powder coating formulations are occurring at a rapid pace. Powders are being developed to compete with almost every market that has traditionally been held by liquid coatings. Factory-applied architectural coatings (based on fluoropolymers), heat resistant coatings, metallic and textured coatings, low-temperature-cure powders, transparent and clear powders, and powders that can be used to color plastic parts by introducing the powder into the mold used for compression-molded plastic are in production use at this time. Most of these developments have occurred during the last several years and most powder coating manufacturers believe that the potential of powder coatings is only beginning to be realized.

In addition to the coating types discussed above, new developments are occurring in the area of enamel powders. Conventional porcelain enamel, the glassy coating traditionally found on metal surfaces such as bathtubs and washing machines, is a vitreous inorganic coating bonded to metal by fusion. The powder coating process for porcelain enamel involves the re-fusing of powdered glass on the metal surface at a cure temperature of 1200°F. The powdered glass is formed by melting oxide components and then quenching to form enamel frits. The frits can be converted to wet sprayable suspensions or to dry enamel powders through ball-milling. The resultant enamel coating is heat stable to over 450°C (842°F), color fast, and scratch resistant.[7] Enamel powders, a potential replacement for porcelain, are now available in a range of colors. Continued development will make these coatings even more competitive.

Polyvinylidene fluoride coatings have recently become available in powder form.[8] These fluoropolymer powder coatings have been available in Europe for about 4 years and are now sold in the United States. Their cure temperature is in the range of 475°-525°F. Because of their high resistance to weathering, industrial pollution, and corrosion, they are factory-applied for use on exterior aluminum extrusions and panels for architectural purposes.

4.0 POWDER COATING EQUIPMENT

The process of applying powder coatings to the surface of a product is, in general terms, similar to the traditional painting line used to apply liquid coatings. For powder coating (or traditional painting), parts to be coated first are exposed to a pretreatment operation to ensure that the

TABLE 1. TYPICAL PROPERTIES OF THERMOSETTING POWDER COATINGS[6]

PROPERTIES	Epoxy	Epoxy/polyester hybrid	TGIC polyester	Polyester urethane	Acrylic urethane
Application Thickness	0.5-20 mils[a]	0.5-10 mils	0.5-10 mils	0.5-10 mils	0.5-10 mils
Cure Cycle (metal temperatures)[b]	450°F - 3 min 250°F - 30 min	450°F - 3 min 325°F - 25 min	400°F - 7 min 310°F - 20 min	400°F - 7 min 350°F - 17 min	400°F - 7 min 360°F - 25 min
Outdoor weatherability	Poor	Poor	Very Good	Very Good	Excellent
Pencil Hardness	HB-5H	HB-2H	HB-2H	HB-3H	H-3H
Direct Impact Resistance, in-lb[c]	80-160	80-160	80-160	80-160	20-60
Adhesion	Excellent	Excellent	Excellent	Excellent	Excellent
Chemical Resistance	Excellent	Very Good	Good	Good	Very Good

[a] Thickness of up to 150 mils can be applied via multiple coats in a fluidized bed.
[b] Time and temperature can be reduced, by utilizing accelerated curing mechanisms, while maintaining the same general properties.
[c] Tested at a coating thickness of 2.0 mil.

surface to be coated is clean and free of grease, dust, rust, etc. In most cases, the parts are also subjected to treatments such as phosphating and chromatizing to improve the adhesion of the surface coating. After pretreatment and drying, the parts enter the spray booth. After the spray coating is applied, parts enter the curing oven to melt and cure the coating.

The following sections present information about the types of equipment that are available for each step in the process outlined above. Numerous manufacturers of powder coating equipment compete in today's market. Each has products that perform the same basic task. The discussions here are generic, in that manufacturers' brand names are not used, and will focus on the spray application of powder to a metal substrate. (Curing ovens used with powder coating systems are similar to those used for liquid coating lines.)

4.1 PRETREATMENT

Although the substrate pretreatment process is critical to achieving an acceptable powder coated finish, the need for good pretreatment is not unique to powder finishes. All industrial surface coatings require a substrate that is clean and dry. A wide range of pretreatment requirements is available for both powder and liquid coatings. The pretreatment process selected is a function of the characteristics of the coating, the substrate, and the end use of the product being coated. The pretreatment process is normally conducted in a series of spray chambers where alkali cleaners, iron or zinc conversion coatings, and rinses are applied. Parts of various size or shape may be cleaned with pressurized and/or heated sprays. Dip tanks may be used instead of spray for some applications. Powder coating lines usually incorporate a phosphate application step that adds corrosion protection and improves the adhesion of the coating to the substrate.

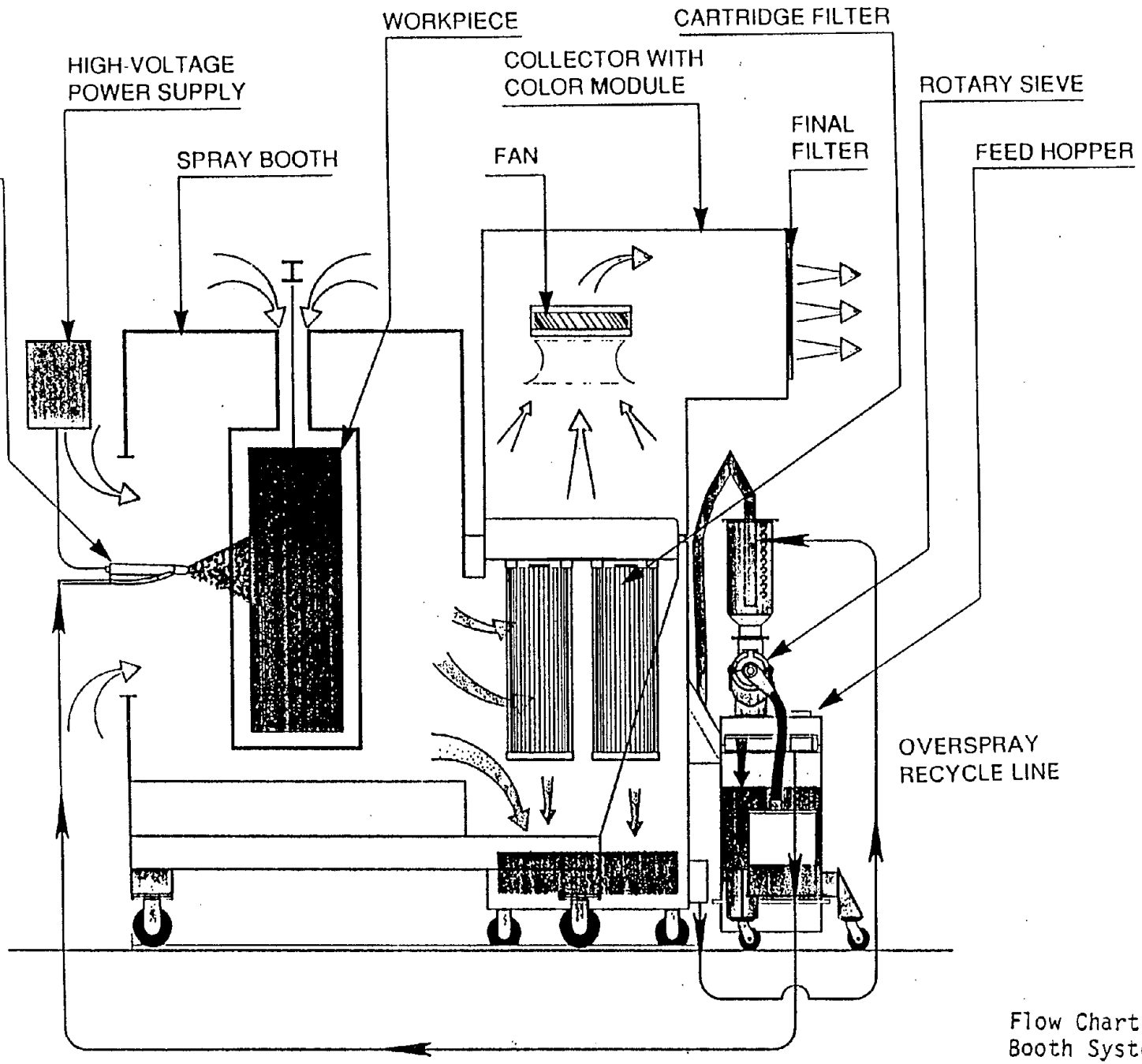
Pretreatments most often used in powder coating are iron phosphate for steel, zinc phosphate for galvanized or steel substrates, and chrome phosphate for aluminum substrates. After the parts have passed through all of the pretreatment steps, they are normally dried in a low temperature dry-off oven. After drying, the parts are ready to be powder coated.

4.2 POWDER APPLICATION

The powder coating application process makes use of four basic types of equipment: the powder delivery system, the electrostatic spray gun system, the spray booth, and the powder recovery system. The flow schematic is shown in Figure 1.

4.2.1 Powder Delivery System

Powder is supplied to the spray gun by the powder delivery system. This system consists of a powder storage container or feed hopper, and a pumping device that transports a mixture of powder and air into hoses or feed tubes. Pneumatic pumps driven by clean, dry compressed air are most often used because they aid in separating the powder into individual particles for easier transport. Each powder pump supplies powder to one gun, typically many feet from the powder supply. Delivery systems are available in many sizes. Proper selection depends on the application, number of guns to be supplied, and volume of powder to be sprayed in a given time period. Recent improvements in powder delivery systems, coupled with better powder chemistries that reduce clumping of the powder, have made possible the delivery of a very consistent flow of particles to the gun. Some feed hoppers vibrate to help prevent clogging or clumping of powders difficult to fluidize prior to entry into the transport lines.



Flow Chart of a Cartridge Booth System

4.2.2 Electrostatic Spray Guns

Electrostatic powder spray guns direct the flow of powder; control the pattern size, shape, and density of the spray as it is released from the gun; impart the electrostatic charge to the powder being sprayed; and control the deposition rate and location of powder on the target. All spray guns can be classified as either manual (hand-held) or automatic (mounted to a fixed stand or gun mover). Both manual and automatic guns are manufactured by many companies. Although their basic principles of operation are similar, there is an almost limitless variety in style, size, and shape. The type of gun chosen for a given coating line can, thus, be matched to the coating characteristics needed for the products being coated.

Most common is for the electrostatic charge to be imparted to the powder particles after they exit the spray nozzle by a charging electrode located at the front of the gun. These "corona charging" guns generate a high-voltage, low-amperage electrostatic field between the electrode and the product being coated. The charge on the electrode is usually negative. Its strength can be controlled by the operator. Powder particles that pass through the ionized electrostatic field at the tip of the electrode become charged. Their flight to the substrate is influenced by the electrostatic field. The particles follow the field lines and air currents to the target workpiece and are deposited on the electrically grounded surface of the workpiece. One drawback to this type of gun is the relative difficulty of coating irregularly shaped parts that have recessed areas or cavities (that may be affected by the Faraday cage effect) into which the electrostatic field lines cannot reach. Because the powder particles are influenced by the presence of the field lines, deposition into recesses and cavities is more difficult, but can be overcome.

Another approach in electrostatic spray guns is the "tribo" electric gun. The powder particles in a tribo electric gun receive an electrostatic charge as a result of friction which occurs when powder particles rub a solid insulator or conductor inside the gun. The resulting charge is accomplished by stripping electrons from the powder, producing positively charged powder. Because there is no actual electrostatic field, the charged particles of powder migrate toward the grounded workpiece and are free to deposit in an even layer over the entire surface of the workpiece. Since there is no electrostatic field, the Faraday cage effect is minimized and deposition into recesses improved. However, each charging technology should be tested to determine the practical application for each unique situation.

Other improvements made to spray guns involve variations in the spray patterns to improve the efficiency with which they deposit powder on the substrate. Nozzles that are more resistant to clogging have also been introduced, along with ways to continuously clean charging electrodes. Spray guns with variable spray patterns are also available to allow the use of one gun on different parts and configurations. Innovations in spray gun design have also resulted in versatile and efficient guns with increased ease of operation. The spray equipment used for manual spraying is simple to control and use. Only a brief period of training is required before the painter can meet quality objectives.

4.2.3 Powder Spray Booths

The primary function of the powder spray booth is to safely contain the powder so that overspray cannot migrate into other areas. Several criteria must be met in selecting the appropriate spray booth for a given coating line. The entrance and exit openings must be properly sized to allow clearance of the largest product part. The airflows through the booth must be sufficient to channel all overspray to the recovery system, but not so forceful that it disrupts the powder deposition and retention on the part. This is usually accomplished by maintaining a minimum average face velocity of 100 ft/min across all end openings. If one

booth is to be used for multiple colors, the booth interior should be free of narrow crevices, seams, and irregular surfaces that would be difficult to clean. This is especially important if collected overspray is to be recycled.

Because there is no solvent loading of the air exhausted from a powder coating booth, the air can be circulated back into the plant. This saves considerable energy during winter months, compared with the energy required to heat makeup air to replace the solvent-laden air flow from a liquid paint booth.[9]

4.2.4 Powder Recovery and Recycle Systems

The powder recovery and recycle systems may or may not be an integral part of the spray booth. The economic efficiencies and environmental benefits associated with reuse of oversprayed powders has led equipment manufacturers to develop systems designed especially to accommodate powder recovery. Traditional spray booths for liquid coatings have either dry or wet filter systems to remove overspray from the exhaust air stream. The collected paint is typically of no value and is therefore discarded, usually at considerable expense since most solvent-based paint overspray meets the RCRA definition of Hazardous Waste.

Recovered powder is of greatest value if free of color contamination. When a single particle of a different color is cured on a part, it will not blend in but remains visible. Numerous systems are now available that segregate colors within the same booth. The systems make use of either cyclones or cartridge filter modules that are dedicated to each color and can be easily removed and replaced when a color change is needed. Color changes can be accomplished by disconnecting the powder delivery system, purging the powder lines, cleaning the booth, exchanging the cyclone canister or filter module used for the previous color with the cyclone canister or filter module for the next color, and connecting the powder delivery system for the new color. Equipment manufacturers have made significant design improvements in powder spray booths that both allow color changes to be made with a minimal downtime and allow the recovery of a high percentage of the overspray. As with spray guns, there are a large number of spray booth and powder recovery designs from which to choose, depending upon the exact requirements of a given finishing system.

4.2.5 Curing Ovens

There are three basic oven types normally used in the curing of powder coated parts: Convection, infrared, or a combination of the two. Convection ovens can be either gas or electric. Air is heated and circulated inside the oven around the powder coated parts. The parts attain the temperature within the oven.

Infrared (IR) ovens using either gas or electricity as their energy source emit radiation in the IR wavelength band. This radiated energy is absorbed by the powder and the substrate immediately below the powder but the entire part need not be heated to cure temperature. This allows a relatively rapid heat rise causing the powder to flow and cure when exposed for a sufficient time.

Combination ovens generally use IR as the first zone to melt the powder quickly. The following convection zone can then utilize rather high velocity currents since there is no danger of disturbing the powder. These higher velocities permit faster heat transfer and a shorter cure time.

4.3 COLOR CHANGEOVERS

Color change in a powder coating system can be accomplished in a relatively short period of time, about one minute when independent booths are moved on and off line. The off-line booth is cleaned while the on-line booth is in production. Adequate time must be allowed to clean an off-line booth before the next color change can occur.

As a result, equipment manufacturers have developed their own approaches to minimizing color change downtime. Color change in an automatic single booth system (eight automatic guns and two manual guns) will generally range from 15 minutes to one hour utilizing two people. Larger systems would require a proportionately longer time.

4.4 TRANSFER EFFICIENCY

Transfer efficiency is generally defined as the ratio of powder deposited on the part or parts to the total amount of powder sprayed. (This fraction is normally multiplied by 100 to express it in percent.) Recovered powder is not considered in this calculation. Many factors can affect transfer efficiency, including proficiency of the operator, shape of the part, booth design, condition of the spray equipment, part grounding, powder condition, and application techniques.

Powder's big economical advantage over liquid paints is that transfer efficiency is not also a measure of paint efficiency. The powder overspray can, with properly designed equipment, be captured and resprayed thereby raising powder utilization to almost 100 percent.

4.5 FILM THICKNESS

Powder coatings can be applied in a wide range of film thicknesses. Continuous films as low as 0.5 mils (0.005") can be applied, as can specialized applications that require as much as 10 mils or more. The very thin films will require special powder grinds. Extremely heavy films are generally achieved by coating the part while it is hot.

The normal range of the vast majority of applications would be 1.0-3.0 mils with an average target value of 1.5 mils. The part's function and its expected environmental exposure will usually dictate the type of coating material to be used and the desired film thickness.

4.6 PROCESS CONTROL IN POWDER APPLICATION SYSTEMS

Process control in powder application systems can be broadly classified into four major categories: gun movement, gun triggering, booth/recovery system monitoring, and flame detection.

The use of oscillators, reciprocators, and robots to control spray equipment reduces labor costs and provides more consistent coverage.

Gun triggering, or triggering the gun on and off using a device that can sense when the target is properly positioned, will reduce overspray material, which translates into lower material and maintenance costs. Automatic gun triggering can also have other benefits such as improved quality of the finish and reduced film build at edges.

In addition to controlling the gun functions, other booth and recovery system variables such as moisture in the air supply, powder level in the feed hopper, and routine diagnostic variables can be monitored using either a microprocessor or programmable logic controllers (PLC's).

Finally, it is mandatory in the U.S. that automatic systems include a flame detection device interlocked with the high-voltage power supply, conveyor, and application and recovery equipment. These devices cut off all electrical and pneumatic supplies within one-half second after detecting an ignition.

4.7 POWDER STORAGE AND HANDLING

Coating manufacturers recommend that powders be stored at temperatures below 80°F and for a maximum of six months.

5.0 END USES OF POWDER COATINGS

As can be seen in Table 2[10], the list of products currently being powder coated is extensive. There are certain market sectors where powder coatings have shown particularly strong growth rates. For example, powder coatings are being used extensively to produce linings on the inside of oil drilling pipe where severe pressures, high temperatures, and corrosive materials are too aggressive for all but a few types of coatings. The automotive industry is increasing its use of powder coatings for economic, quality, and ecological reasons. Powder is being used by some manufacturers for the exterior body intermediate coat - the primer-surfacer - as well as for finishing of underhood components. Parts that require extra protection as well as a decorative finish are increasingly being powder coated. Wheels, bumpers, shock absorbers, mirror frames, oil filters, engine blocks, battery trays, and coil springs are some of the many automotive products being powder coated. Clear powder coatings, for use over automotive exterior basecoats, are now being developed for commercial application as an alternative to solvent-borne clear coats.

The appliance industry is the largest single market sector for thermosetting powders, accounting for about 21 percent of powder sales.[11] As porcelain-replacement powders become further developed, the appliance market will continue to grow. Current uses include range housings, freezer cabinets, dryer drums, and washer tops and lids.

Outdoor furniture, farm implements, and lawn and garden equipment are also major markets for powder coatings. The general metal finishing industry accounts for about 53 percent of thermoset powder sales.[11] (The general metal finishing industry is defined here as including all metal finishing industries except for the automotive, appliance, architectural, and lawn and garden finishing industries.)

Potential large market areas for powders are the aluminum extrusion and architectural products markets. The recent advances in polyester-TGIC and fluoro-polymer powders have enabled powder coatings to compete with liquid architectural coatings in durability, weatherability, and resistance to fading. Some of these coatings applied to building panels have been out in the field in Europe since 1976 with good results.

The custom coating sector is one of the fastest growing segments of powder coating, meeting the need for most of the sectors mentioned above. Of the estimated 3,000 powder coating systems in use in North America, 900 are custom coaters.

The Powder Coating Institute estimates that powder coating use in North America will grow from 74,560 tons in 1992 to about 117,946 tons in 1996. During this period, the projected

TABLE 2

END USES FOR THERMOPLASTIC AND THERMOSET POWDERS

METAL SUBSTRATES

AUTOMOTIVE EXTERIOR:
Wheels
Luggage racks
Window trim
Truck tool boxes
Windshield wipers
Bumpers
Rally (roll) bars
Mirror brackets
Primer surfacer
Anti-chip primers
Radio antennas
Door handles
Air louvers

AUTOMOTIVE INTERIOR:
Ash trays
Speaker covers
Defroster vents
Steering wheels
Seat pedestals
Seat belt latches/mounts
Jacks/lug wrenches
Truck seat frames

AUTOMOTIVE UNDERBODY:
Engine blocks
Radiators
Suspension systems
Coil springs
Shock absorbers
Oil/air filters
Motor mounts
Intake manifolds
Valve covers
Brake assemblies
Battery trays
Pulleys
Fuel injector tubes
A/C components
Small motor components

METAL SUBSTRATES

AUTOMOBILE MISC.:
Boat trailers
Trailer hitches
Mobile home doors/windows
Motorcycles

MAJOR APPLIANCES:
Gas & electric ranges
Range hoods
Refrigerator doors, shelving, liners, & skins
Washer tops & lids
Dryer drums
Freezer cabinets
Water heaters

FURNITURE-HOME:
Bunk beds
Patio furniture
Kitchen tables/chairs
Chair frames & bases
Baby strollers/swings/ playpens, etc.
Folding chairs/tables
Barbecue grills
Metal cabinets
Bookends
Wire baskets

FURNITURE-COMMERCIAL/INSTITUTIONAL:
Chair bases/frames
Office partitions
Filing/storage cabinets
Lockers
Wastebaskets
Dentist chairs
Hospital beds
Examination tables
Copier cabinets
Stadium seating

SHELVING & RACKING:
Retail store shelving
Retail store racks
Point-of-display racks
Warehouse rack systems

METAL SUBSTRATES

HEATING/VENTILATION/AIR COND.:
Central A/C cabinets
Window A/C cabinets
Gas/electric furnace cabinets
Swimming pool heaters
Evaporation coolers
Space heaters
Air cleaners

INDUSTRIAL EQUIPMENT/MACHINERY:
Industrial mixers
Grain storage systems
Animal feeding units
Thickness gauges
Friction disk binders
Vending machines
Ice making machines
Irrigation pipes
Pay phones/booths
Electrostatic spray equipment
Escalator steps
Battery chargers
Air compressors
Pressure reserve tanks
Fans, shutters, louvers
Gas & electric meters
Drum rings
Food processing carts
Lobster traps
Hand trucks
Gasoline pumps
Sonar equipment

LAWN & GARDEN:
Riding mowers
Walk-behind mowers
Edgers
Fertilizer spreaders
Snowblowers
Garden tillers
Chain saws
Tractors

(continued on next page)

TABLE 2 (Continued)

END USES FOR THERMOPLASTIC AND THERMOSET POWDERS

METAL SUBSTRATES

HARDWARE:
Brass & metal door hardware
Brass bathroom fixtures
Closet organizers
Wire & metal shelving
Drapery hardware
Shower curtain hardware
Safe deposit boxes
Wine racks
Christmas tree stands
Notebook spiral wires
Luggage frames
Desk accessories
Mechanical pens/pencils
Thumbtacks
Wire cloth/screens
Water pumps
Water tanks
Steel drums
Scaffolding
Military hardware
Door thresholds
Alarm system bells
Propane tanks
Draw slides/suspension units
Camp stoves
Grapevine support poles
VCR cases
Water cans
Mailboxes
Screen doors
Aluminum doors/windows
Metal doors
Antennas
Gas cans
Pool hardware
Highway & other signs
Fence wire & poles
Guard rails
Building facade panels
Satellite dishes
Fire extinguishers
Parking meters
Aluminum extrusions
Post-formable tubing
Ornamental iron security doors

METAL SUBSTRATES

TOOLS:
Tool boxes & chests
Hand tools
Snowplow blades
Power tools
Steel carts
Hand trucks

LIGHTING FIXTURES:
Fluorescent lighting fixtures
Decorative lighting fixtures
Desk lamps
Yard lights
Light poles
Outdoor lighting fixtures

SMALL APPLIANCES:
Kitchen blinds
Kitchen mixers
Crock pots
Vacuum cleaners
Can openers
Floor care machines
Cigarette lighters
Microwave oven cavities
Fans
Speaker frames
Microphones
Tape player doors
Computer frames/cabinets
Bathroom scales
Automatic timers

SPORTS/RECREATION:
Playground equipment
Recreation vehicle hardware
Bicycle frames/wheels
Gas/electric golf carts
Golf clubs
Snowmobiles
Ski poles & ski parts
Metal toys
Wagons
Marine motors & drives
Archery bows
Exercise equipment

METAL SUBSTRATES

ELECTRIC COMPONENTS:
Motor windings & housings
Magnet wire
Electrical motor - stators/rotors
Computer room floor sys.

ELECTRICAL EQUIP.:
Transformers
Switch gear
Electric junction boxes
Electric connectors
Buss bars
Electrical instrument housings/cabinets

OTHER FUNCTIONAL COATINGS:
Petroleum transmission pipes
Oil well drilling pipes
Reinforcing bar for concrete
Rebar saddles
Cable for prestressed concrete
Structural steel
Conduit
Truck splines
Dishwasher baskets
Military projectiles

NON-METAL SUBSTRATES

CERAMICS:
Decorative glass bottles
Flash bulbs
Instrument bulbs
Roofing tile

WOOD:
Toilet seats

PLASTIC:
Sinks/shower stalls
Automotive fascias
Automotive dashboards

annual growth rate for selected market areas is: automotive-9%, appliance-11%, architectural-9.5%, lawn and garden products-8%, and general metal finishing-12 %.[11]

6.0 ECONOMIC ADVANTAGES OF POWDER COATING VS. LIQUID COATINGS

When comparing powder coating systems with liquid coating systems, several significant advantages are readily apparent. There are also other, seemingly less significant advantages that, when viewed collectively, contribute substantial cost savings. This section discusses the economic advantages of powder vs. liquid coating systems in the following areas: energy savings, labor savings, greater operating efficiencies, and environmental benefits. A detailed cost comparison of powder vs. liquid coating systems also is provided at the end of this section.

6.1 ENERGY SAVINGS

There are two significant advantages of powder coating which contribute to lower energy costs as compared to liquid coating. The first is that the air used to exhaust the powder spray booth can be recirculated directly to the plant since the powder does not contain volatile compounds at room temperature. This eliminates the cost of heating or cooling the makeup air that occurs when air is exhausted from the plant with liquid spray painting operations, a particular advantage where seasonal weather conditions are extreme. The second advantage is the lower cost of heating the curing oven. Ovens that cure solvent-based coatings must heat and exhaust huge volumes of air to ensure that the solvent fumes do not approach the lower explosive limit. Because powder coatings have no solvent content, the required exhaust flow in the curing ovens is considerably lower resulting in energy savings even when higher cure temperatures are involved.

6.2 LABOR SAVINGS

The required operator skills and training for operation of a powder coating system are less than those needed for a liquid system and considerably less than those required for an electrocoat system. Powder is "ready to use" when purchased and does not require labor for mixing with solvents or catalysts as is necessary with liquid coatings. Also, there are no critical operating parameters to monitor such as viscosity and pH (which are monitored in many liquid coating systems) or percent solids, specific resistance, and binder to pigment ratio, (which all must be monitored in electrocoating systems). Additionally, powder systems lend themselves well to automation. Since powder coatings do not run, drip, sag, or have solvent pops, a wider variety of parts can be coated automatically.

6.3 GREATER OPERATING EFFICIENCY

Because no drying or flash-off time is required, and the powder application system allows parts to be racked closer together on a conveyor, more parts can pass through the production line resulting in greater operating efficiency and lower unit costs. Despite the greater line speeds, powder coating systems generally have significantly lower reject rates than do liquid coating systems. One reason for this lower reject rate is that it is virtually impossible to have drips, runs, or sags when applying powder coatings. Additionally, because booth air exhaust may be returned to the spray room, it is practical to reduce rejects caused by airborne contamination by enclosing the spray room and keeping it under slightly positive pressure while air conditioning and filtering the air. If, prior to entering the cure oven, a powder coated part is found to be improperly sprayed, the powder can be blown off with an air gun and the bare part recoated. Another factor which contributes to a greater operating efficiency is the fact that oversprayed powder can be reclaimed and reused, and material usage is minimized.

6.4 ENVIRONMENTAL BENEFITS

As regulatory agencies further limit the amount of solvent and hazardous air pollutants (HAP's) that can be emitted, many plants that use liquid coating systems are finding it necessary to purchase VOC control equipment, such as afterburners, to incinerate the emitted solvents and HAP's. Another environmental problem faced by liquid coating users is the increased difficulty and cost of disposing of hazardous waste generated by liquid coating overspray. With a dry powder coating system, there is no liquid paint sludge to send to a disposal site.

6.5 COST COMPARISON: POWDER VS. LIQUIDS

A detailed cost comparison between powder and liquid coating systems is provided below. The three types of liquid coating systems included in the comparison are: conventional solvent, water-borne, and high solids. Total capital and annual operating costs are provided for each of the four coating systems. Material costs represent two-thirds or more of the total annual operating costs, and therefore, detailed material costs are also provided.

6.5.1 Total Capital Costs

Capital costs for four different coating systems (i.e. conventional solvent, water-borne, high solids, and powder) are presented in Table 3. The source of these costs is a reprint from Products Finishing entitled "Powder Coating Advantages" (1991), generated by The Powder Coating Institute.[12] "Powder Coating Advantages" is an updated version of the 1987 publication "Powder Coating Today." These cost estimates are consistent with estimates provided by powder coating equipment suppliers in response to questionnaires submitted by the EPA.

Powder coating equipment that cost $150,000 in 1983[13] could be purchased for $145,000 in 1990. The "Powder Coating Advantages" article includes a carbon absorber in the cost of the conventional solvent-borne liquid coating system.

The capital costs presented in Table 3 are based on the following assumptions:

1. The parts to be coated are formed sheet steel parts that are of average complexity;
2. Both sides of each part are automatically coated and touched up manually;
3. Two colors are used;
4. There is a production rate of one million square feet of surface coated per month based upon a five-day week, one-shift operation;
5. Conveyor speed is 15 ft/min;
6. The installation is new and has automatic equipment to efficiently apply either a conventional solvent, water-borne, high solids, or powder coating;
7. A carbon absorber for emission compliance (cost $96,000) is added to the system applying conventional solvent-borne coatings to satisfy emission regulations; and
8. The same pretreatment systems and ovens can be used with each system with little or no modification.

6.5.2 Material Costs

Materials costs for the four coating systems are presented in Table 4; these costs are based on two different sources of information. Both sources calculated the material costs in a similar manner with the higher solids system generally having a lower unit volume material cost. The most complete and up-to-date source of cost information is the aforementioned "Powder Coating Advantages" article (Reference Nos. 15 and 17 in Tables 4 and 5). Costs obtained

TABLE 3. TOTAL CAPITAL COSTS[12]

Type of Coating	Equipment	Capital Cost
Conventional Solvent	2 Waterwash Booths	$115,000
	1 Dry Filter Booth	
	8 Automatic Guns	
	2 Manual Guns	
	2 Reciprocators	
	Paint Heating Equipment	
	Carbon Absorber for Emission	$ 96,000
	Compliance	$211,000
	Total	
Water-borne	2 Waterwash Booths	$120,000
	1 Dry Filter Booth	
	8 Automatic Electrostatic Guns	
	2 Manual Electrostatic Guns	
	2 Reciprocators	
	Safety Interlocks and Standoffs	
High Solids	2 Waterwash Booths	$115,000
	1 Dry Filter Booth	
	8 Automatic Electrostatic Guns	
	2 Manual Electrostatic Guns	
	2 Reciprocators	
	Paint Heating Equipment	
Powder	1 Booth with 50 sq. ft. opening	$145,000
	8 Automatic Guns	
	2 Manual Guns	
	2 Reciprocators	
	2 Reclaim Stands with Automatic Reclaim	
	2 Collectors	
	Fire Detection	

TABLE 4. MATERIAL COSTS, DOLLARS

Item	Ref. #	Conventional Solvent	Water-borne	Higher Solids	Powder[a]
Coating cost, $/gal	(14)	---	---	21.00	2.40
	(15)	11.00	12.40	17.25	2.35
Volume solids, %	(14)	---	---	54	98
	(15)	43	35	63	98
Reducing agent cost,	(14)	---	N/A	N/A	N/A
$/gal	(15)	2.00	N/A	N/A	N/A
Mix ratio (coating:	(14)	---	N/A	N/A	N/A
reducing agent)	(15)	4:1	N/A	N/A	N/A
Mixed coating costs,	(14)	---	---	21.00	2.40
$/gal	(15)	9.20	12.40	17.25	2.35
Volume solids at	(14)	---	---	54	98
spray viscosity, %	(15)	34.4	35	63	98
Specific gravity	(14)	---	---	---	1.6
	(15)	---	---	---	1.6
Theoretical coverage,	(14)	---	---	866	118
ft^2/gal/mil	(15)	552	561	1,011	118
Dry film thickness,	(14)	---	---	1.2	1.5
mils[b]	(15)	1.0	1.0	1.0	1.5
Transfer efficiency,	(14)	---	---	80	95
%[c]	(15)	45	55	60	96
Actual coverage,	(14)	---	---	577	75
ft^2/gal	(15)	248	309	607	76
Applied cost, $/ft^2$	(14)	---	---	0.0364	0.0320
	(15)	0.0371	0.0401	0.0284	0.0309
Annual cost to coat	(14)	---	---	436,800	384,000
$12x10^6$ ft^2, $	(15)	445,200	481,200	340,800	370,800

[a] Substitute pounds for gallons in all calculations.

[b] Coating thicknesses were normalized to put costs on a common basis.

[c] Transfer efficiency is the ratio of coating that adheres to the part and the coating that is sprayed through the gun. In the case of powder coating, where powder is recovered and recycled, the term "utilization efficiency" is used.

from the User's Guide To Powder Coating (1987) (Reference No. 14) were included in Tables 4 and 5 for comparison purposes. (Note that in Table 4, the columns for powder costs are in terms of lb. rather than gal.)

The material costs presented in Reference Nos. 15 and 17 are based on 1990 data and the following assumptions:

1. The conventional solvent-borne baking enamel price represents a material with 43 percent (by volume) solids applied at an average thickness of 25 μm (1.0 mils);
2. The water-borne acrylic price is based upon a 35 percent (by volume) solids material applied at an average thickness of 25 μm (1.0 mils);
3. The higher solids coating is a general purpose polyester at 63 percent solids applied at an average thickness of 25 μm (1.0 mils); and
4. The powder coating is a general-purpose polyester powder applied at an average thickness of 30 μm (1.2 mils).

These dry film thicknesses were set at levels that are believed to be representative of current industry practices.

6.5.3 Total Annual Operating Costs

The total annual operating costs for the four coating systems are presented in Table 5. All literature references used to create Table 5 identified powder coating as having the lowest annual operating costs. The highest operating costs were associated with the conventional solvent or water-borne coating systems. Labor, cleanup, maintenance, energy, and waste disposal costs were lowest for the powder coating system, which contributed to overall lower annual operating costs. The "Powder Coating Advantages" article (Reference No. 17) again provided the most complete and up-to-date information on annual operating costs. The operating costs presented in that brochure are based on 1990 data and the following assumptions:

1. Labor costs $14.55 per hour and supervision costs $18.45 per hour;
2. Cost of electricity = $0.085 per kWh;
3. Cost of natural gas = $3.23 per thousand ft^3; and
4. Removal of nonhazardous paint sludge was estimated to cost $300 per 55-gal drum.

The material costs for any of the four coating systems could be less than those shown if either the volume solids and/or transfer efficiency is increased and/or the film thickness lowered. For example, if the transfer efficiency for the higher solids case (Reference 15, Table 4) is increased from 60 to 70 percent, the annual materials cost to coat will drop from $340,800 to $292,500. The annual cost to coat = [(coating thickness) (mixed coating cost) (surface area coated per year)] / [(theoretical coverage) (utilization efficiency)]. Likewise, if the powder coating thickness in Reference 15 (Tables 4) were decreased from 25 to 20 μm (1.0 to 0.8 mils), the material cost would drop from $340,800 to $272,970.

It should be noted that, currently, the minimum consistent powder coating film thickness is in the range of 10-15 μm (.5 mil). If the product can perform satisfactorily with a thinner film, the extra cost of applying more powder than necessary should be considered when comparing alternative coatings.

TABLE 5. TOTAL ANNUAL OPERATING COSTS, DOLLARS[a]

Item	Ref. #	Conventional Solvent	Water-borne	Higher Solids	Powder
Material, $/yr	(16)	---	---	436,800	384,000
	(17)	445,200	481,200	340,800	370,800
Labor and clean-up, $/yr	(16)	---	---	111,400	85,200
	(17)	160,200	160,200	160,200	98,600
Maintenance, $/yr	(16)	---	---	11,840	5,060
	(17)	29,300	29,300	29,300	17,000
Energy, $/yr	(16)	---	---	38,474	34,905
	(17)	21,400	22,800	19,900	11,525
Sludge disposal, $/hr	(16)	---	---	8,460	N/A
	(17)	50,100	33,300	27,300	975
Filter replacement, $/hr	(16)	---	---	1,920	N/A
	(17)	---	---	---	---
Amortization, 10-yr straight line, $	(16)	---	---	---	---
	(17)	21,100	12,000	11,500	14,500
Total annual cost, $[b]	(16)	---	---	594,670	497,310
	(17)	727,300	738,800	589,900	513,400
Applied cost, $/ft²	(16)	---	---	0.0508	0.0425
	(17)	0.0606	0.0616	0.0491	0.0428

[a] Assumed 2,000 operating hours per year.
[b] Numbers have been rounded.

7.0 CONCLUSIONS

The use of powder coatings as functional and decorative industrial finishes is increasing at a dramatic rate. At an annual rate of 12 percent, powder coating is the fastest growing finishing technology on the market.[1] (Sales volumes of powder coatings are much smaller than liquid coatings, so a direct comparison of growth rates is not meaningful.) Significant improvements in powder coating materials and application, and powder recovery systems have made powder one of the most cost effective finishing systems available. In addition, because powder coatings contain no solvents and overspray can be recovered and recycled, air and water pollution problems are eliminated in well-operated facilities. Energy costs attributable to heating and ventilation are significantly reduced.

The use of powder coatings as an alternative to liquid, solvent-based coatings results in a significant decrease in VOC and HAP emissions. Powder coatings can be characterized as the lowest VOC-content coating among the compliance options available to industrial finishers. Table 6 presents a VOC reduction comparison of the four coating systems reviewed in Section 6. The values in this table were based on the average of the values presented in Table 4. As shown in Table 6, VOC emissions for powder coating systems are 98.4 percent lower than those for conventional solvent coating systems, 98.1 percent lower than those shown for higher solids systems, and 97.7 percent lower than for water-borne systems.

Most of the drawbacks to the use of powders that existed a few years ago (see Section 2) have been eliminated. New resin systems allow powders to meet the coating specifications for almost any application. Thin films (from less than 25 um [1 mil] to about 76 um [3 mils]) in a very wide range of colors, glosses, and textures can be applied at powder utilization rates of 95 percent or higher.[18] Many of these coatings can be cured at temperatures of 121°C to 177°C (250°F to 350°F) in 15 to 30 minutes.[6] Powder manufacturers are continuing to work toward perfecting resin and curing agent designs that will allow lower cost coatings and low temperature cure coatings. Low temperature curing powders allow for higher line speeds, and expand the list of potential substrates to plastics, wood, and heat sensitive products like automobile shock absorbers.

Significant advancements are also being made in the weatherability of powders for use in automotive and architectural applications. Clear powder coatings are used for a wide range of applications in a number of markets, including the automotive industry, where clear polyester and acrylic powders are being used to finish wheels. Powder resin systems are now available that provide the exterior durability properties required of an automotive exterior body topcoat.

Recent and ongoing developments in the equipment used for powder application have significantly reduced the time, effort, and capital cost required for color changes. Properly designed powder systems can change colors in minutes. Currently, high-production powder systems apply more than 20 different colors, with several color changes per day.[19]

Coil coating technology for powder continues to be developed. Coil coating is the coating of flat metal sheet or strip that comes in rolls or coils. The metal is coated on one or both sides on a continuous production line basis.

An in-mold powder coating process has been developed in which powder coating material is sprayed onto a heated mold cavity before the molding cycle begins. When the molding operations are performed, the powder coating chemically bonds to the molding compound and

produces a product with a coating that is chip and impact resistant.

The powder coating of pre-cut metal blanks which are then post-formed prior to final assembly remains a strong growth area for powder, with high transfer efficiency and uniform film thickness. [20]

Advances in microprocessors, robotics, and infrared curing technology are allowing increased production in powder coating facilities. All of these advances, plus the inherent advantages of working with powder, ensure that powder coatings will have a permanent and ever-increasing share of the finishing market.

TABLE 6. VOC REDUCTION COMPARISON[a]

	Conventional Solvent	Water-borne	Higher Solids	Powder Coating
Volume solids at spray viscosity, percent[b]	34.4	35	58.5	98
Volume VOC content, percent [c] [d]	67	16	40	1
Actual coverage, ft^2/gal (ft^2/lb for powder)[e]	248	309	592	75.5
VOC emissions, tons/yr[f]	38	26	31	0.6

[a] Assumed $12x10^6$ ft^2 of parts coated per year.
[b] Average of values presented in Table 4b.
[c] Assumed density of solvent equals 7.36 lb/gal.
[d] Water-borne coating VOC content assumed to be 25 percent of the nonsolids portion.
[e] Average of values presented in Table 4b. Based on transfer efficiencies presented in Table 4b.
[f] Control device assumed for conventional solvent with overall efficiency of about 70 percent (based on capture efficiency of about 75 percent and destruction efficiency of about 95 percent). All other systems assumed to have no control device.

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CHLORINATED-MALEINIZED GUAYULE RUBBER IN POWDER COATINGS: NO VOC THERMOSETTING CHLORINATED RUBBER COATINGS

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INTRODUCTION

Chlorinated rubber, the addition and substitution reaction product of natural rubber and chlorine gas, is known for its low water vapor permeability, good chemical resistance, abrasion resistance, corrosion resistance, and flame retardant properties.[1] Consequently, it is used as a coating component in a variety of coating applications including marine coatings, swimming pool coatings, and corrosion resistant coatings.[2] However, the use of chlorinated rubber in coating compositions has declined in recent years primarily because chlorinated rubber coatings must be cast from volatile organic compounds (VOCs), and the films formed possess poor solvent resistance. Therefore, we have created a novel, multi-functional derivative of chlorinated rubber for use in low VOC formulations. Specifically, this investigation describes the synthesis of anhydride functionalized chlorinated rubber and its utilization in powder coatings and contributes to other recent work in this area.[3-6]

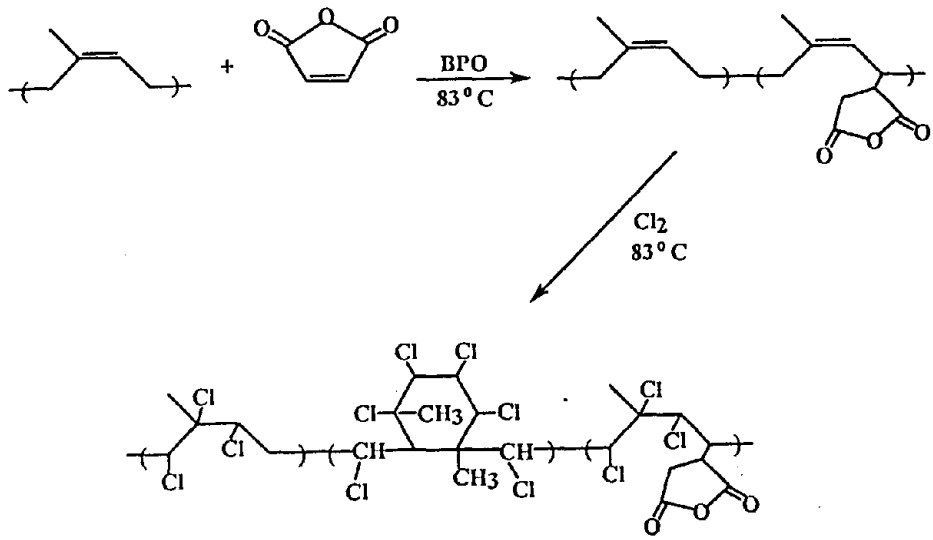
The powder coatings industry has experienced significant growth since its inception, and by all accounts this trend is expected to continue. Growth in powders is due in large measure to its environmental advantages of low to no VOC emissions. Thus, by 1988, the annual growth rate was 23% in the United States alone.[7] Accordingly, as powder coatings reach toward new technological heights and thus new applications, there is need for additional polymer systems to meet specific performance requirements.

Powder coatings formulated from chlorinated rubber (CR) have received little or no attention in the literature. Presumably, this is due to poor thermal properties. For instance, CR has high glass transition temperatures (>100°C) and undergoes decomposition prior to melting.[8] When used alone, it performs poorly as a powder coating resin. Polymers with a low melt viscosity are desirable as powder coating resins in order to obtain adequate film coalescence, good flow, and adhesion. Thus, melt temperatures of 50 to 100°C are attractive as they are easily processed at low costs. Thus, we have investigated polymer blends as an approach to partially stabilize an otherwise thermally unstable CR.

Chlorinated rubber blends of alkyd resins, acrylics, epoxy esters, epoxy resins, hydrocarbon resins, rosins, and tars have been used successfully in solvent cast coatings and give desirable film properties representing an amalgamation of resin types.[8] Thus, blending novel crosslinkable CR with functionalized powder coating resins was an attractive concept to the design and synthesis of no VOC, CR, powder coatings.

We have previously reported the synthesis of chlorinated-maleinized guayule rubber (CMGR), a thermosetting CR derived from guayule natural rubber. The synthesis was accomplished by grafting maleic anhydride (MA) onto unsaturated sites with the subsequent chlorination of residual double bonds.[9] (See Figure 1.)

Figure 1: Synthesis of Chlorinated-Maleinized Guayule Rubber



Variations in the stoichiometric quantities of maleic anhydride grafts have been affected to produce a myriad of chlorinated-maleinized rubber crosslinkable agents. Chlorine, as a part of the rubber composition, dramatically improves water resistance, chemical resistance, and flame resistance. On the other hand, the anhydride moiety effectuates crosslinking via covalent bond formation and thereby improves a number of polymer properties, not the least of which is solvent resistance. Thus, this novel material shows unusual promise as a CR additive in thermosetting powder coatings, and it is to this end that this research was focused.

EXPERIMENTAL PROCEDURES

Materials

Crude low molecular weight guayule rubber (LMWGR) and resinous byproduct was obtained from Bridgestone/Firestone, and the LMWGR was separated from plant resin by continuous acetone extraction. The rubber was further purified by the addition of a 10% (w/w) toluene solution of rubber to an equal or greater volume of methanol. Reagent grade MA, benzoyl peroxide, chlorine, and 1,2-dichloroethane were purchased from Aldrich and used as received. Primid XL-552, a hydroxy alkyl amide supplied by Rohm & Haas, functioned as the powder coating curative. Modaflow Powder III obtained from Monsanto Company was added to the powder formulations to improve flow. Schweizerhall, Inc. supplied benzoin, a degas agent, and McWhorter Technologies supplied 30-3070, an acid-functional polyester resin. For the analysis of CR, samples of Alloprene R-20 provided by ICI Resins, Inc., were utilized.

Synthesis of Chlorinated-Maleinized Guayule Rubber

A 50 gram sample of purified rubber was dissolved in 1,2-dichloroethane to a 2% (w/w) concentration, and placed in a 3000 ml three-neck round bottom flask equipped with a mechanical stirrer, addition funnel, thermometer, gas dispersion tube with a scintered glass end, and condenser. The amount of MA for the desired degree of maleinization was added to the flask as a solid. Nitrogen was bubbled through the solution for 10 min to sparge the remaining oxygen. The contents of the flask were heated to reflux (83°C), during which time a 250 ml 1,2-dichloroethane solution of benzoyl peroxide was added dropwise with caution over a 30 min period. Reflux continued throughout the grafting and chlorination reactions. After 3 h, chlorine gas was introduced into the reactor at a rate of 0.2-0.3 g/min until a total of 90 g of chlorine was added. Chlorination was affected via a lecture bottle equipped with

teflon tubing, and the weight loss of the bottle was monitored with a Mettler PM3000 balance. The solution was cooled, concentrated *in vacuo*, and the product isolated by the addition to 2000 ml of stirring methanol followed by vacuum filtration. The product, a coarse yellow powder, was further purified by dissolution in toluene followed by precipitation into methanol. After drying overnight *in vacuo*, a fine light-yellow product is obtained.

Equivalent Weight Analysis

Samples were weighed to four significant figures and dissolved in a blend of 100 ml of toluene and 25 ml of isopropanol. Titration with phenolphthalein indicator was affected against a 0.1040 M solution of potassium hydroxide in methanol and the equivalent weight per carboxylate (EWC) was determined using Equation 1:

$$EWC = W/(2VK) \quad [1]$$

where W = weight of specimen, V = ml of KOH to neutralize, and K = moles KOH/ml of solution. In the denominator, the two accounts for only ½ of the carboxylate of the anhydride is measured via this method. The percent grafting efficiency was determined on samples prior to chlorination by comparing the calculated equivalent weight to the theoretical equivalent weight assuming stoichiometric conversion as represented by Equation 2.

$$GE = (\text{Theoretical EWC}/\text{Calculated EWC}) * 100 \quad [2]$$

Characterization of CMGR and CMGR Powder Coatings

For infrared analysis, samples were cast onto sodium chloride discs from tetrahydrofuran and dried *in vacuo* for 30 min. Fourier transform infrared (FTIR) spectroscopic analysis was performed on a Nicolet IR/42 Spectrophotometer. Thermal properties were monitored via a Mettler DSC 30 equipped with liquid nitrogen subambient cooling. The temperature profile of analysis included heating the samples from room temperature to 100°C at 10°C/min cooling to 0°C at 10°C/min and finally heating to 300°C at 10°C/min to complete the cycle. TGA weight loss analysis was recorded on a Mettler TGA 50 under an air atmosphere. Samples were heated from 30°C to 500°C at 20°C/min. Environmental scanning electron microscopy (ESEM) was obtained from an Electroscan Type II ESEM. The coatings were evaluated according to ASTM standards as listed in Table I.

Table I: CMGR Coating Tests

Test	ASTM
Impact Resistance	D-2794
Conical Mandrel	D-552
Crosshatch Adhesion	D-3359
Pencil Hardness	D-3363
MEK Double Rubs	D-4752
8 Hour Spot Tests	D-1308
Film Thickness	D-1186
Gloss	D-523
Salt Fog Exposure	B-117

Gel time analysis was performed on a Thermoelectric Company cure plate at 188°C. Samples weighing 1 g were added to the cure plate and the time required for sample gelation was recorded.

Formulation of Chlorinated-Maleinized Guayule Rubber Powder Coatings

Chlorinated-maleinized guayule rubber of 5% MA content was blended with a commercially available polyester-polyamide powder coating at 4, 6, and 10% (w/w). To affect good mixing, CMGR and the reactive polyester (30-3070) were dissolved in THF at room temperature, the solvent was removed *in vacuo* at 40°C, and the residual powder was dried overnight before mix extrusion.

A stoichiometric balance of 1:1.01 of the CMGR/polyester blend and the curative (primid xl-552), respectively, was confirmed by titration of each of the reactants.

All formulations (Table II) were mix processed and extruded according to parameters listed in Table III.

Table II: Powder Coating Formulations

Material (g)	Control	4% CMGR	6% CMGR	10% CMGR
30-3070	282.21	260	251.01	228.5
CMGR	---	20	30	50
Primid XL-552	11.8	12.27	13	13.45
Benzoin	2.59	2.59	2.59	2.59
Modaflow III	3.75	3.75	3.75	3.75
Dupont R-960	199.65	199.65	199.65	199.65
Total	500	500	500	500

Table III: Processing Parameters

Premix	
Henschel FM-10 C	
120 sec at 2000 RPM	
Extrusion	
Werner & Pfleiderer ZSK 30	
Screw Temperature	113°C
Die Temperature	113°C
Load on ZSK 30	30%
Speed	300 RPM
Chill Rolls	
Temperature	55°C
Roll Speed	45 Hz

The final particle size was obtained by grinding on a Micron Powder Systems Model SH Bantam Mill and sifting through 110 micron mesh on a Kem-U-Tech Laboratory Sifter. The powders were sprayed onto cold rolled steel panels with a Nordson Corona Model NVC 4 Spray System, and cured in a Despatch Gas Oven at 325°C for 20 min.

RESULTS AND DISCUSSION

Chlorinated-Maleinized Guayule Rubber

Chlorinated-maleinized guayule rubber containing 5, 10, 15, and 25 mol% MA was synthesized according to the synthetic scheme of Thames and He (Figure 1). Titration prior to chlorination confirms a grafting efficiency greater than 85% with averages of 90%. The products, fine light-yellow powders, were analyzed by thermal, titriometric, and infrared analysis.

The products were titrated to determine the acid value or equivalent weight with varying MA content. Accordingly, the results of Table IV confirm increasing acid value and decreasing equivalent weight as the MA content increases.

Table IV: Selected Properties of Chlorinated-Maleinized Guayule Rubber

% MA	Acid Value	EWC	T_g
0%	---	---	115°C
5%	42	1,352g/COOH	166°C
10%	65	866g/COOH	148°C
15%	91	614g/COOH	158°C
25%	113	495g/COOH	159°C

The glass transition temperatures (T_g) of the CMGR compositions of Table IV ranged from 158°C to 166°C. While maleinization increases the T_g of CR, no consistent relationship between MA content and T_g was apparent. The variation in thermal characteristics with maleinization is illustrated in Figure 2. The gradually increasing exotherm beyond 210°C is presumably due to slow decomposition of CMGR.

Infrared analysis corroborates the structural similarity of CMGR and CR, yet with the addition of the anhydride functionality. For instance, the FTIR spectrum for CMGR and CR shown in Figure 3 suggests structural likeness through comparable IR absorption frequencies. While for the most part the spectra are similar, variations occur via absorptions in the 1650 cm^{-1} - 1850 cm^{-1} and approximately 700 cm^{-1} regions. In the latter instance, the absorption is consistent with carbonyl stretching of the anhydride moiety. The split absorption is indicative of atmospheric hydrolysis of the anhydride to acid moieties. This feature is further noted with the broadening of the aliphatic C-H absorption of CMGR at 3500 - 2500 cm^{-1}. The absorption at approximately 700 cm^{-1} in the CR spectrum is indicative of C-Cl stretching. Other minor spectral differences can be attributed to the anhydride functionale of CMGR. Hence, titriometric, thermal, and infrared analysis confirm the successful synthesis of chlorinated-maleinized rubber.

Figure 2: DSC Thermograms for Chlorinated-Maleinized Guayule Rubber and Chlorinated Rubber

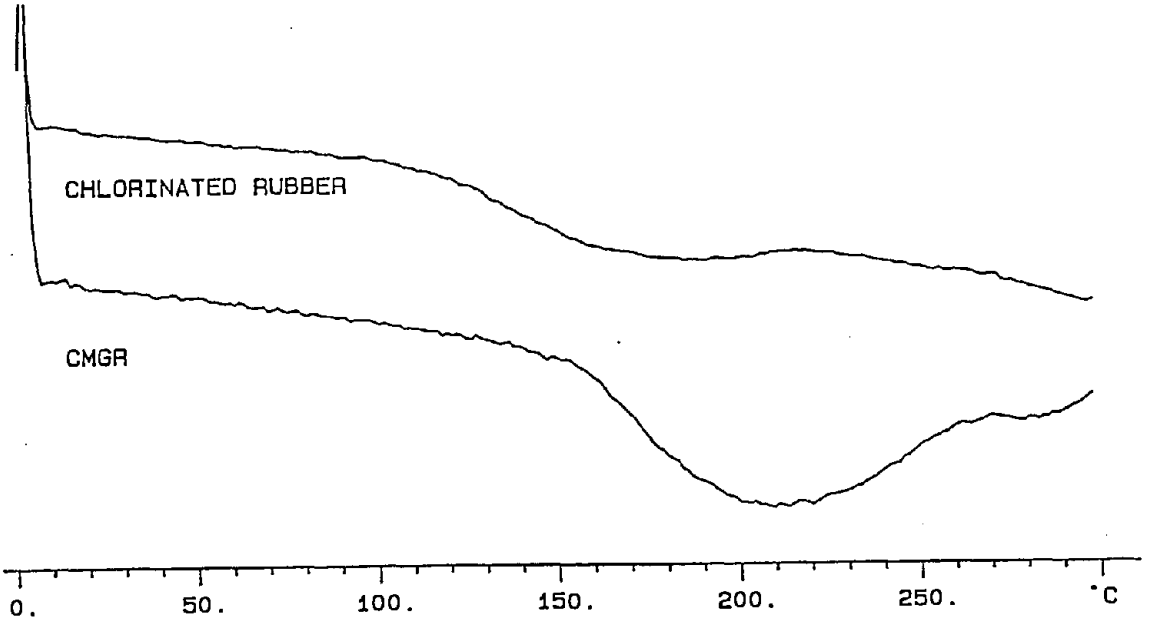
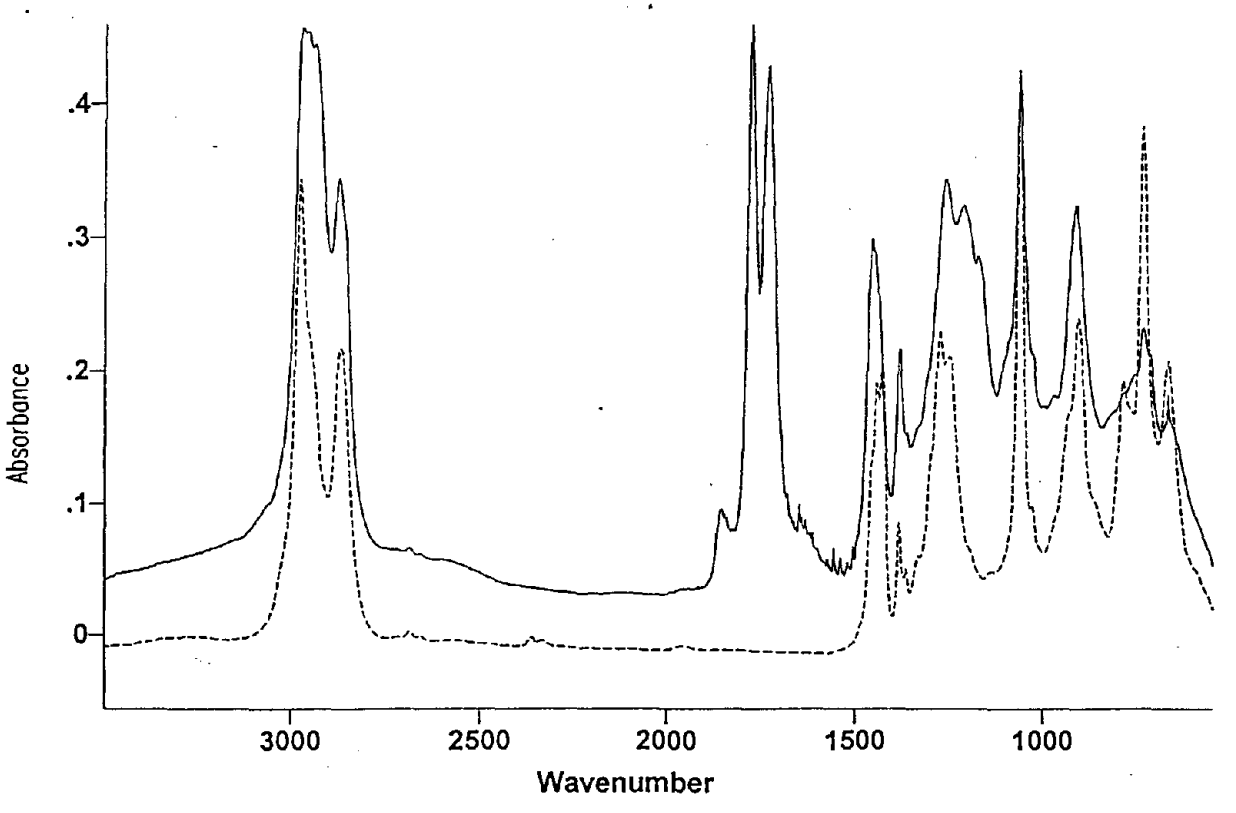


Figure 3: FTIR Spectrum of Chlorinated-Maleinized Guayule Rubber and Chlorinated Rubber



Chlorinated-Maleinized Guayule Rubber Powder Coatings

Having confirmed the synthesis of CMGR and its similarity to CR, we turned our attention to the use of these materials in powder coatings, their application, and coatings evaluation. Powder coatings containing 4, 6, and 10 wt% CMGR were formulated, applied, cured, and evaluated.

The data of Table V is instructive in confirming film property variations attributable to CMGR. For instance, with increasing anhydride functionality gel time diminished as expected, coating hardness increased and MEK resistance increased up to a 6% use level of CMGR. However, MEK double rubs, and NaOH resistance suggest strongly that coatings formulated with 10% CMGR contain unreacted acid functionality. For instance, the reduction in MEK resistance from 140 to 135, the dramatic gloss reductions, and the diminished NaOH resistance suggest an excess of carboxylate functionality.

Table V: Powder Coating Properties

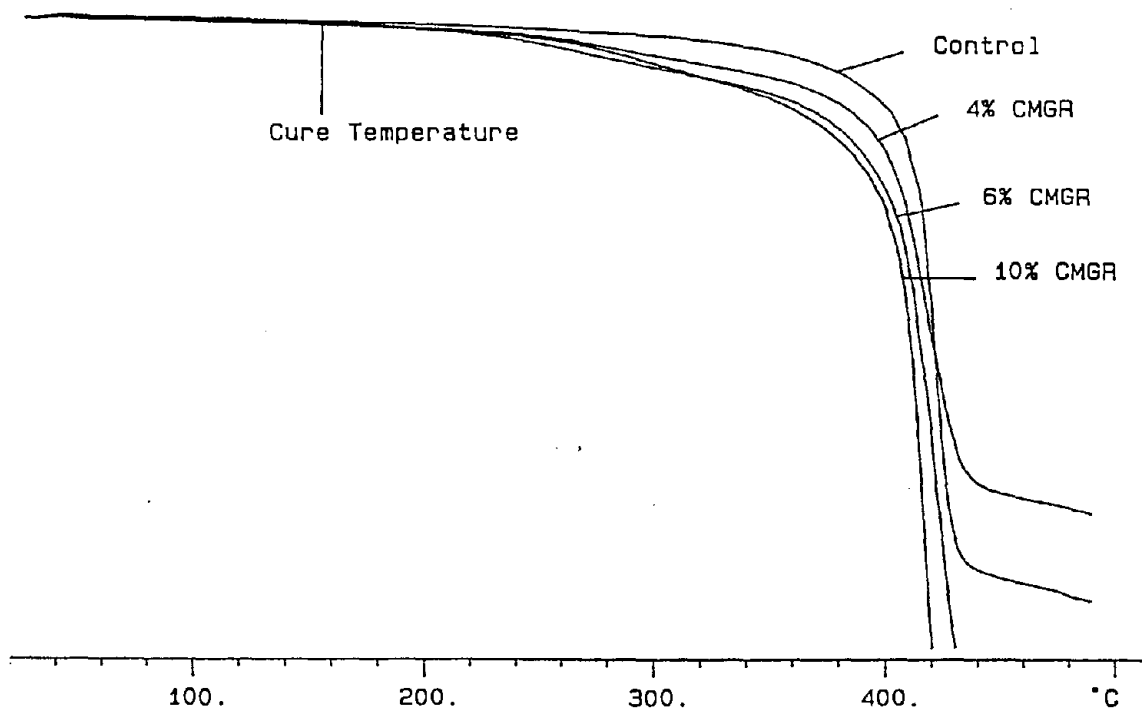
Test	Control	4% CMGR	6% CMGR	10% CMGR
Thermal Properties				
T_g	59°C	54°C	56°C	54°C
Gel Times at 188°C	141 sec	104 sec	69 sec	63 sec
Average Film Thickness	2 mils	2 mils	2 mils	2 mils
Impact Resistance				
Forward (in-lb)	160	160	160	160
Reverse (in-lb)	140	140	160	160
Conical Mandrel	Pass	Pass	Pass	Pass
Crosshatch Adhesion	5B	5B	5B	5B
Pencil Hardness	2H	5H	6H	8H
MEK Double Rubs	50	110	140	135
Gloss (20/60)	55/85	33/72	20/55	1/5
8 Hour Spot Tests[a]				
20% Sulfuric Acid	5	5	5	5
10% NaOH	5	5	5	4
Conc. NH_4OH[b]	5	5	5	5
Water	5	5	5	5
150 Hour Salt Fog	Pass	Fail	Fail	Fail

a - 5= no effect 4= stain only 3= blistering 2= lifted film 1= failure
b - 30% NH_3 by weight

Coatings containing CMGR are light tan in color while the control was white. This color variation is suggestive of thermal decomposition or oxidation of the CMGR, yet TGA analysis showed essentially no weight change at the curing temperature (Figure 4). Thus, the slight discoloration is

consistent with the off-white color of CMGR. The TGA profiles for the control and the CMGR coatings (Figure 4) are quite similar with only slight variations in the thermal decomposition as the CMGR content is increased. TGA analysis confirms the beginning of thermal decomposition near the 250°C region. Gloss reduction was progressive with the addition of CMGR and at 10% (w/w) CMGR coatings took on a low gloss, textured finish. The dramatic gloss loss with increasing amounts of CMGR is indicative of high melt viscosities and/or a heterogeneous medium produced by excessive, and thus unreacted, functionality. The textured appearance of coatings formulated with 10% CMGR, whether due to changes in melt viscosity or phase separation, gives them a unique, attractive appearance.

Figure 4: TGA Analysis of Powder Coatings



While gel time, pencil hardness, solvent resistance, and reverse impact improved with the addition of CMGR, corrosion resistance declined. This is suggestive of diminished flow and wetting associated with the addition of CMGR. Indeed, the ESEM corroborated a crack-marred surface, and thus porous films that allow moisture penetration and consequently corrosion.

CONCLUSIONS

Chlorinated-maleinized guayule rubber, a novel chlorinated rubber bearing acid anhydride functional sites, has been synthesized and employed in a number of powder coating formulations. The incorporation of the acid anhydride functionality to CR was confirmed by infrared analysis and titration.

Powder coatings blended with CMGR showed improvements in cure rate, solvent resistance, pencil hardness, and reverse impact while adhesion,

flexibility, and chemical resistance were retained. Formulations of powder coatings containing alloprene, a commercially produced CR, gave similar results, but lacked the solvent resistance of the CMGR coatings. However, the CMGR led to gloss reductions and at a 10% level, an attractive, low gloss, textured finish was obtained. Of more concern, however, is the observed poor corrosion resistance believed to be a function of film porosity. Thus, the overall utility of CMGR as a powder coating reagent requires additional formulation variations and perhaps CMGR structural variations in order to enhance flow and wetting characteristics.

This work has confirmed for the first time the utility and shortcomings of CMGR as a reactive polymer in powder coating formulations. We will continue this investigation in pursuit of high performance and durable CMGR powder coatings.

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NOVEL ACRYLIC CURE POLYESTER POWDER COATING RESIN TECHNOLOGY

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INTRODUCTION

Increasingly stringent environmental regulations within the industrial finishing industry have caused coatings formulators to focus on the development of technologies that meet the dual requirements of environmental compliance and high performance. Powder coatings, as a result, are enjoying double digit growth as industrial finishers look for ways to meet these challenges.

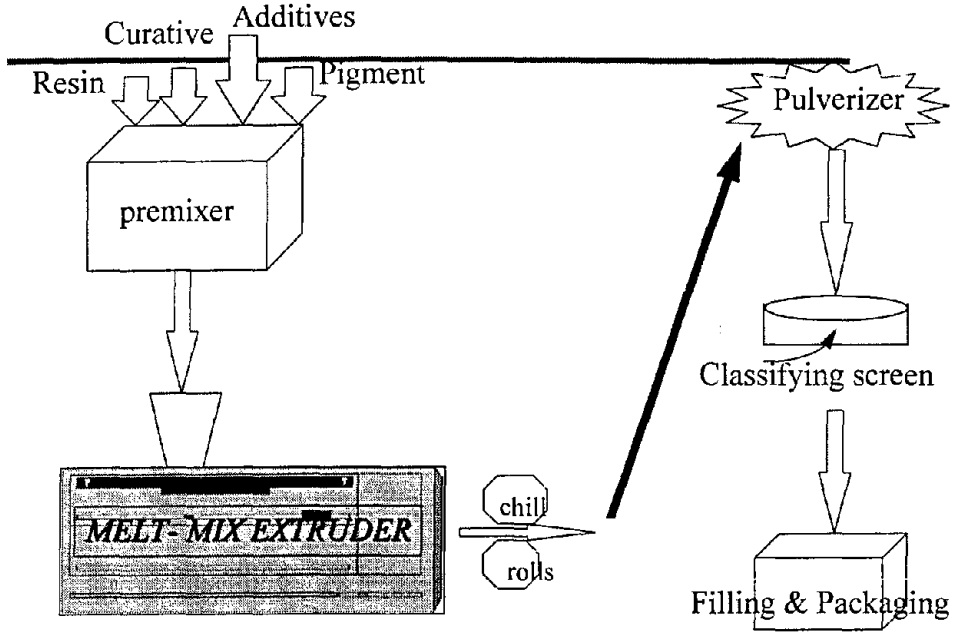
Powder coatings have been projected to account for **15 %** of the overall North American industrial finishing market by the end of the decade. [1] As powder replaces traditional liquid paint technologies on an ever-increasing basis, tougher performance standards for powder coatings are being demanded. These new conditions have led to the development of novel powder coating resin technology that offers the formulator an excellent approach to meeting the needs of today's challenging coatings environment.

POWDER COATINGS BACKGROUND

Powder coatings, unlike conventional liquid paint technologies, contain no solvents (100 % solids), and are virtually 100 % VOC free. A major benefit is its' high material utilization rate. Oversprayed powder can be reclaimed and, after mixing with virgin powder, can be reused. Other economic advantages of powder are the reduced costs of waste disposal and pollution control. (There is no liquid paint sludge, and spray booth air can be recycled to the plant facility.) Additionally, the choice of color is as varied as in liquid coatings, and special effect finishes are also possible through the use of various additives.

A typical powder coating consists of a thermosetting resin, crosslinker, flow and levelling agents, pigmentation, and inorganic fillers. These solid materials are premixed either in low or high intensity mixing equipment prior to being melt-mixed in a compounding extruder. During the extrusion process, the resinous mixture is heated above its' melting point and made homogeneous through mechanical shear. Therefore, proper temperature/shear relationship is key to obtaining optimum dispersion of the coating's components. The molten extrudate is usually cooled by the use of chill rolls, or a cooling belt, whereby it is converted into a crushable ribbon. This ribbon is then pulverized and classified to the desired particle size for application. For general metal applications, a 40 micron average particle size powder coating is common. **Figure 1** shows a schematic representation of a continuous powder coating production process.

FIGURE 1 Powder Manufacturing Process



The powder can subsequently be applied to a grounded metal substrate with an electrostatic (corona charging) spray gun. Other application methods are also possible: tribocharging, whereby the powder particles receive a frictional charge as they pass through the spray apparatus, and fluidized bed dipping. Tribocharging is suitable for metal fabrications that have unusual geometries, and would therefore be vulnerable to Faraday cage effect. [2] Fluidized bed dipping is utilized in applications such as pipe coatings that require film thicknesses in excess of 10 mils. The final step in the process is the curing of the powder coating. This can be accomplished by gas or electric convection ovens, infrared cure, or a combination of both convection and radiation. During the cure cycle, the powder fuses, melts, and flows to form a continuous film. After a suitable cure cycle, the coating will have developed a highly crosslinked system, with the resultant physical properties.

Powder coating technologies can be broadly classified as either thermosetting or thermoplastic. Thermoplastic powders, the oldest powder coatings technology, include materials such as nylon and polyvinyl chloride. Unlike the particle size mentioned above, the thermoplastics have a much larger average particle size (> 100 microns), as it takes much more energy to grind them.[3] After the initial cure cycle they can be remelted if desired, and will solidify upon cooling. Thermosetting powders, conversely, cannot be remelted once they have undergone cure. The materials that are used for these powder coating vehicles (resin and crosslinker) are usually high molecular weight, crystalline polymers. They must have a careful balance of rheological and reactive properties. Additionally, they must be low enough in T_g to have suitable flow properties, but at the same time, be stable under long-term storage conditions. The thermosetting variety are more widely used, comprising approximately 91 % of current U.S. powder consumption. [4]

The thermosetting chemistries can be grouped as epoxies, polyesters, epoxy-polyester hybrids, and acrylics. As is the case with other coatings technologies, each powder chemistry has its' inherent advantages and disadvantages. The oldest thermosetting powder technology involves the use of epoxy resins which are diglycidyl ethers of bisphenol A (DGEBA), crosslinked with amines, anhydrides, dicyandiamide, or linear phenoic curatives. While this system has excellent corrosion and chemical resistance, its' exterior durability and overbake resistance is poor.

Saturated polyester resins followed, and a host of curing agents are commercially available for these polymers. These polyesters are generally classified as carboxyl fuctional or hydroxyl functional.

The carboxy polyesters can be cured with epoxy functional resins. These systems are referred to as polyester-epoxy hybrids, and are characterized by very good film smoothness and mechanical properties. They also exhibit the problems associated with straight epoxy systems, that is, fair to poor exterior durability. One system that does offer excellent exterior durability features a trifunctional curative- triglycidylisocyanurate, or TGIC. However, recently published toxicity data has raised some health concerns for personnel using this material. [4] Generally, an overall advantage of the epoxy/carboxy crosslinking mechanism is that it proceeds by addition, hence no volatiles are evolved during the cure cycle.

Hydroxyl functional polyester resins can be crosslinked with several different hardeners, the most widely used being blocked isophoronediisocyanate (IPDI). Epsilom caprolactam is typically the blocking agent used in the IPDI prepolymers. Coatings made with these materials are referred to as polyurethanes and exhibit good film smoothness, exterior durability, storage stability, and mechanical properties. Disadvantages of polyurethanes include elevated bake temperature requirements ($> 350^{0}$ F), and the evolution of small amounts of volatiles during cure. A portion of the blocking agent sublimes during the cure process. In inadequately vented ovens, it appears as a bluish haze, and is perceived to be a health hazard. The effectiveness of infrared curing lamps can also be decreased as the $\sum$ -caprolactam accumulates on the heating surfaces. As more powder coatings end-users utilize IR curing, solutions to this problem will need to be developed. Possibly as a proactive measure, a growing number of urethane users are requesting "$\sum$ -caprolactam-free" coatings, without sacrificing the performance benefits of smoothness and flexibility normally associated with this technology. One such alternative will be discussed in this paper.

Another major class of powder coatings are the acrylics. They can be hydroxy, carboxy, or glycidyl functional. The crosslinking of these resins occurs much in the same fashion as their polyester analogues. The OH and COOH acrylics can be cured with the same materials as the polyesters. However, they have not seen the same acceptance as the polyesters due to poorer mechanical properties and high cost vs. the polyesters.

The glycidyl functional acrylics have seen recent growth because of their excellent exterior durability, relatively low cure temperatures (300^{0} F), and film smoothness. Acrylics based upon glycidyl methacrylate (GMA) crosslinked with linear dibasic acids such as dodecanedioic acid (DDDA) have been found to be the highest performing thermoset powder coating in terms of exterior durability and acid rain resistance. This technology does have a few disadvantages, however. GMA acrylics usually have lower mechanical properties such as flexibility and impact resistance than polyesters. Additionally, formulated GMA acrylic/DDDA powder coatings (or "pure" acrylics) typically exhibit incompatibility with other powder coating chemistries. A polyester coating contaminated with less than 1 % of a GMA acrylic coating will cause massive film defects (i.e. cratering). It is not the acrylic component that

induces the incompatibility, but rather the use of siloxane flow modifiers within the acrylic powder coating that give the undesired result. The observed cratering is the end result of the large surface tension gradient between the polyester and acrylic films.

Researchers at Reichhold Chemicals, Inc. and its' parent company, Dainippon Ink and Chemicals (DIC) of Japan, have sought to develop unique resins for the powder coatings industry that would help overcome some of the above mentioned problems and disadvantages, while advancing the state-of-the-art in powder coating technology.

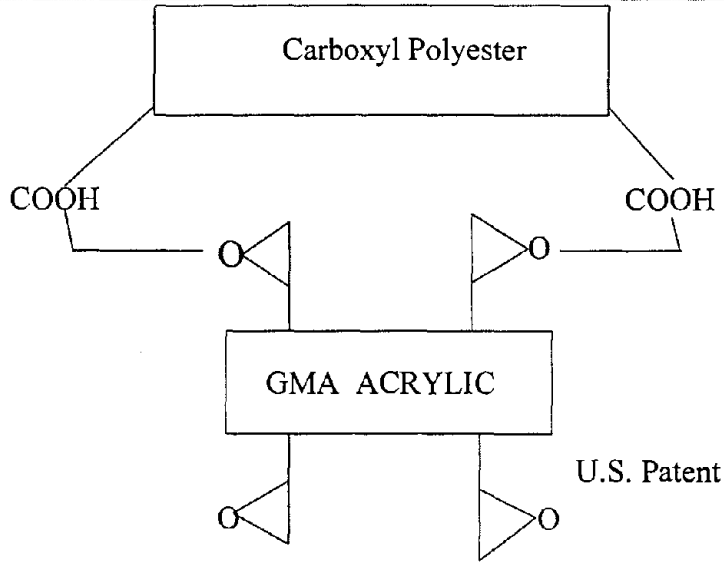
Two examples of our progress here include the development of high performance coatings for precoated metal (PCM) and development of powders with extremely low gloss that are highly reproducible. The new resins should also find utility in general metals applications that require a high level of performance.

DEVELOPMENT OF NOVEL CURING MECHANISMS

A novel acrylic cure technology has been developed that features the crosslinking of carboxyl functional sites on polyester resins with glycidyl methacrylate (GMA) acrylic curing agents. This addition chemistry, referred to as an acrylic/polyester hybrid, has inherent advantages over the conventional carboxy/glycidyl powder technologies described previously in that it combines good exterior durability with lower associated health risks. This curing mechanism produces uniform, high-gloss finishes with film smoothness comparable to that of a standard TGIC-cured coating. At the same time, it can be considered an alternative to $\sum$ -caprolactam-containing urethane powder coatings. The curing mechanism is shown in **Figure 2**.

ACRYLIC CURE POLYESTER

FIGURE 2

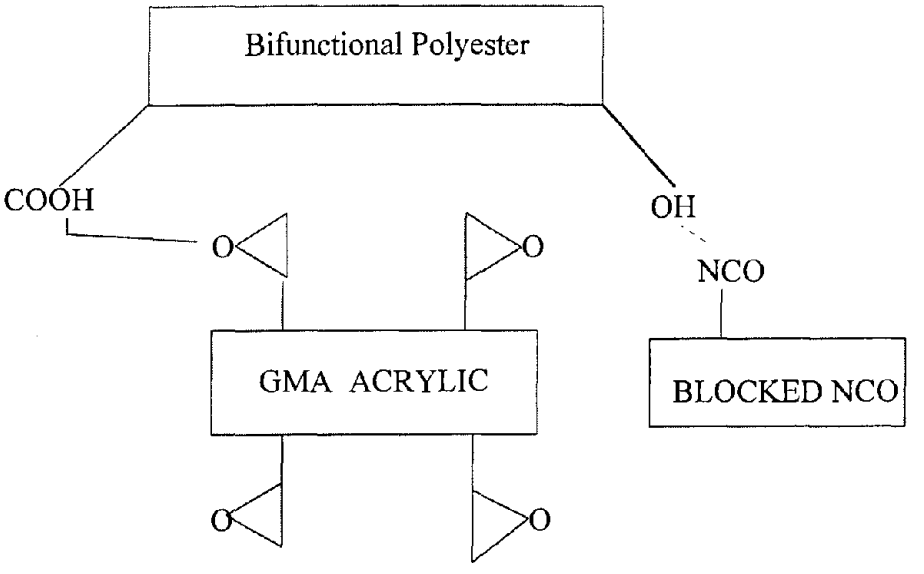


U.S. Patent 4,499,239

A second curing mechanism similarly involves the utilization of GMA acrylic curing agents with a polyester resin that has bifunctionality, that is, there are both carboxyl and hydroxyl groups available for crosslinking. An isocyanate is used here to react with the OH groups of the polyester. However, the required amount is much less than the standard polyurethane, so the associated volatile level is lower. **Figure 3** shows the curing mechanism for this system. Again, coatings based on this approach show good film smoothness, mechanical properties, and very good exterior durability.

MULTI-CURE ACRYLIC/POLYESTER

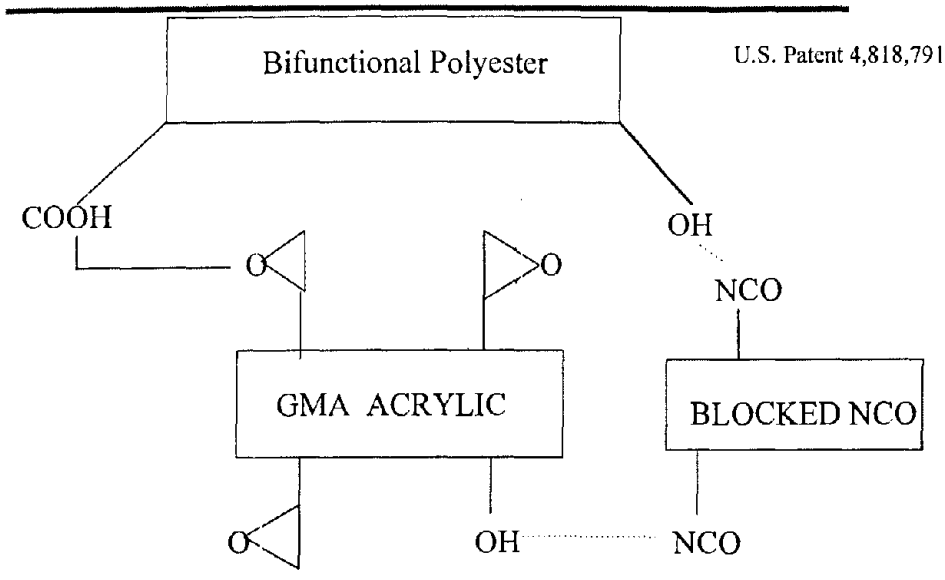
Patent Pending **FIGURE 3**



A third approach also uses the bifunctional polyester. As before the carboxyl groups of the polyester react with the oxirane groups of the acrylic curing agent, and the hydroxyl/isocyanate reaction takes place. However, the GMA acrylic hardener in this case also has OH groups, and these can also react with the NCO curative. This curing mechanism is referred to as a multi-crosslinking system. It has a high crosslink density and exhibits the benefits of urethane and acrylic chemistries. Although slightly more blocked isocyanate is used in this system, it is still less than would be found in a conventional polyurethane powder coating. Formulated coatings based on these materials exhibit excellent smoothness, flexibility, chemical and stain resistance, as well as good exterior durability. With this balance of properties, the bifunctional polyester/acrylic has the attributes necessary to satisfy most coating service environments. The reaction diagram for this system is shown in **Figure 4.** Formulations for the three acrylic/polyester systems are listed in **Table 1,** with their corresponding cured physical properties listed in **Table 2.** It should also be noted that these acrylic/polyester curing mechanisms do not cause the contamination problems associated with "pure" GMA acrylic powder coatings.

MULTI-CROSSLINKING ACRYLIC CURE POLYESTER

FIGURE 4



PRE-COATED METAL FINISHING

Pre-coated metal (PCM), or blank, finishing technology has been established commercially in Southeast Asia and Europe for several years, and is now being developed in North America. The concept is similar to liquid coil coating, in that it involves the coating of flat steel stock. However, powder coating of blanks gives edge coverage usually not associated with liquid coil coating.

Blanks are cut to size, holes punched in the blanks, and then the piece is powder coated. After the coating has cured, the blank is formed into the shape of a refrigerator, laundry machine, or file cabinet, for example. Since the blanks are subjected to large amounts of bending, (also called post-forming) excellent flexibilty is a prerequisite for the applied powder coating. Additionally, the appliances will ultimately be exposed to severe operating conditions, (washing machines, for instance) and the powder coatings applied to these products must have superior resistance to detergents and other chemicals that can stain or damage the finished product. For these reasons, the above mentioned multi-crosslinking technology (**Figure 4**) is an excellent approach to this new coating process.

A unique feature of blank lines is that they typically use infrared cure technology. Gas convection curing dominates the general metal finishing markets, but infrared cure is preferred for the PCM process because of its' efficient mode of heat transfer. Unlike convection curing, which cures the coating by transferring heat from the substrate to the film, infrared energy is absorbed directly by the coating. Also, the IR energy must "see" the material that it is targeted for. Therefore, the simple geometry of a PCM application line is well-suited for IR cure. With this arrangement, it has been found that the blocking agent in urethane coatings is not suitable for IR ovens, and hence a new challenge for the PCM market has occurred. That is, PCM-grade coatings are most desirable when they are $\sum$ -

caprolactam-free. The commercially available internally-blocked ($\sum$ -caprolactam-free) IPDI crosslinker, because of its' higher melt viscosity and slower reactivity, generally gives powder coatings with poorer film appearance and lower mechanical flexibility. Multi-crosslinking powder coatings formulated with this $\sum$ -caprolactam-free isocyanate exhibit only minor decreases in film appearance while still retaining their post-formability. **Table 3** shows a physical property comparison of multi-crosslinking power coatings with $\sum$ -caprolactam blocked IPDI and $\sum$ -caprolactam-free IPDI.

LOW-GLOSS POWDER COATINGS

Interest in low-gloss powder coatings continues to increase, particularly in the area of exterior durable coatings. Reproducible low-gloss coatings are well-established in the epoxy and epoxy-polyester hybrid coating technology segments.[5] However, for exterior applications, these chemistries are not suitable because of their tendency to easily chalk and yellow.

Previously, methods for producing exterior durable powders relied upon the use of flattening agents such as silica, or by dry-blending polyester powders of differing reactivities together. Such techniques have frequently resulted in an inconsistent matte appearance, or have been dependent upon carefully controlled extrusion and curing conditions. The dry-blending method has also been shown to be quite labor intensive and impractical when carried out in a production environment.

The novel acrylic cure powder coating resin technology is well-suited for this coatings challenge. Both the carboxy polyester/GMA acrylic and bifunctional polyester/GMA acrylic/NCO (multi-cure) systems can be produced in a full range of gloss, from matte to high gloss, with excellent smoothness and mechanical properties. In addition, these systems have excellent gloss stability over a wide range of cure cycles. By varying the ratio of the GMA acrylic hardeners- Fine-Clad® A-249-A and A-229-30-A for the bifunctional polyester type, Fine-Clad®A-244-A and A-229-30-A for the carboxy polyester type- a consistent and predictable gloss level is achieved. **Tables 4** and **5** display powder coating formulations and physical property test data for the multi-cure systems in a full range of gloss. **Table 6** illustrates the linear relationship between GMA acrylic hardener ratios and 60^0 gloss in these prepared powder coatings. **Table 7** displays the gloss stability of a formulated matte finish (**Formulation I -Table 4**) for a time/temperature cure matrix. This gloss stability is especially critical for end-users that paint substrates of varying mass on the same finishing line, where actual metal temperatures may widely fluctuate.

CONCLUSION

Industrial finishing is changing rapidly. Today's strict environmental laws pose significant challenges for coatings end-users. Powder coatings have demonstrated their capabilities as environmentally sound alternatives to the traditional solvent-borne coatings technology. The novel acrylic cure polyester approach presented here allows the industrial finisher to apply superior coatings, while significantly reducing waste and VOC-type pollution. The acrylic/polyester approach provides state-of-the-art performance in the new pre-coated metal/blank, low-gloss, and exterior durable polyester arenas.

ACKNOWLEDGEMENTS

The author wishes to thank his co-workers who contributed to this paper: Richard Kittle, Richard Hong, Andrew Woo, and Dr. Hirofumi Takeda.

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TABLE 1: ACRYLIC/POLYESTER FORMULATIONS

DESCRIPTION	"ACRYLIC CURE"	"MULTI-CURE"	"MULTI-X-LINKING"
Formula No.	**1**	**2**	**3**
FINE-CLAD® M-8400 Carboxy Polyester (1)	80.0	-	-
FINE-CLAD® A-239-J Bifunct.Polyester (1)	-	76.0	-
FINE-CLAD® A-239-X Bifunct.Polyester (1)	-	-	72.5
FINE-CLAD® A-229-30-A GMA Acrylic (1)	20.0	15.0	-
FINE-CLAD® A-244-A GMA Acrylic (1)	-	-	11.0
Hüls B-1530 IPDI (E-caprolactam blocked)	-	9.0	13.5
Actiron DBT (2)	-	0.6	0.3
Modaflow 2000 (3)	1.5	1.5	1.5
Benzoin	0.5	0.5	0.5
TiO_2	43.0	43.0	43.0

(1) Reichhold Chemicals, Inc.

(2) Dibutyl Tin Dilaurate- Synthron, Inc.

(3) Monsanto, Inc.

TABLE 2 : PHYSICAL PROPERTIES FOR ACRYLIC/CURE POLYESTERS

DESCRIPTION	"ACRYLIC CURE"	"MULTI-CURE"	"MULTI-X-LINKING"
FORMULA NO.	1	2	3
Baking Schedule, min./^{0}F	10/400 ^{0} F	10/400 ^{0} F	10/400 ^{0} F
Film Thickness,mils	2.5	2.1	2.4
Gloss,60^0/20^0	91/66	91/62	93/82
"b" value	0.35	-0.14	0.7
PCI Flow Rating (1-10) 10=Best	3	4	6
Pencil Hardness	H	H	2H
Gardner Impact:F/R (5/8"), IN.-LBS.	40/20	60/60	120/120
Mar Resistance	Excellent	Good	Excellent
Crosshatch Adhesion	100%	100%	100%
Solvent Cure Test-PCI # 8 B- (1)	part./full cure	part./full cure	Full cure
Inclined Plate Flow (PCI # 7), mm	50 mm	85 mm	100 mm
Gel time (PCI #6), seconds	30-35 sec.	65-70 sec.	45-50 sec.
100 % Overbake Resist., Gloss 60^0/20^0	90/63	88/58	92/75
100 % Overbake Resist., "b" value	0.65	0.16	1.4
Delta b	0.3	0.3	0.7
Xenon Arc Weather-o-meter Exposure: % Gloss Retention after 500 hours	65%	75%	50%

(1) Powder Coating Institute Test # 8B: 100 Double Rubs with MEK

TABLE 3: MULTI-CROSSLINKING POWDER COATINGS:
COMPARISON OF ∑ -CAPROLACTAM-containing and ∑ - CAPROLACTAM-free coatings

	A	B
FINE-CLAD ® A-239-X Bifunct.Polyester (1)	72.5	72.5
FINE-CLAD ® A-244-A GMA Acrylic (1)	11.0	11.0
Hüls B-1530 IPDI (E-caprolactam blocked)	13.5	-
Hüls BF-1540 (E-caprolactam-free)	-	14.4
Actiron DBT (2)	0.3	1.5
Modaflow 2000 (3)	1.0	1.5
Benzoin	0.5	0.5
TiO_2	43.0	43.0

(1) Reichhold Chemicals, Inc.

(2) Dibutyl Tin Dilaurate- Synthron, Inc.

(3) Monsanto, Inc.

Baking Schedule, min./^{0}F	10/400 ^{0} F	10/400 ^{0} F
Film Thickness,mils	2.4	2.3
Gloss,$60^0/20^0$	93/82	91/58
"b" value	0.7	0.3
PCI Flow Rating (1-10)	6	5-6
Pencil Hardness	2H	2H
Gardner Impact:F/R (5/8"), IN.-LBS.	120/120	60/60
Mar Resistance	Excellent	Fair
Crosshatch Adhesion	100%	100%
Solvent Cure Test-PCI # 8 A- (4)	Full cure	partial cure
Inclined Plate Flow (PCI # 7), mm	100 mm	99 mm
Gel time (PCI #6), seconds	45-50 sec.	95-100 sec.
100 % Overbake Resist., Gloss $60^0/20^0$	92/75	88/49
100 % Overbake Resist., "b" value	1.4	1.4
Delta b	0.7	1.1
Flexibility: T-Bend	2T	5-6T

(4) Powder Coating Institute Test # 8B: 100 double rubs with MEK

TABLE 4: POWDER COATING FORMULATIONS FROM MATTE TO HIGH GLOSS

	Formulas I-VI: Bifunctional Polyester/GMA Acrylic/ IPDI;					
	I	II	III	IV	V	VI
	Parts by weight					
FINE-CLAD ® A-239-X Bifunct.Polyester (1)	64.5	64.5	64.5	64.5	64.5	64.5
FINE-CLAD® A-229-30-A GMA Acrylic (1)	0.0	8.0	10.0	12.0	14.0	16.0
FINE-CLAD® A-249-A GMA Acrylic (1)	24.0	12.0	10.0	8.0	6.0	4.0
FINE-CLAD® M-8400 Carboxy Polyester (1)	-	-	-	-	-	-
FINE-CLAD ® A-244-A GMA Acrylic (1)	-	-	-	-	-	-
Hüls B-1530 IPDI	12.0	16.0	16.0	16.0	16.0	16.0
Dodecanedioic Acid (2)	1.5	1.5	1.5	1.5	1.5	1.5
Actiron DBT (3)	0.2	0.4	0.4	0.4	0.4	0.4
C_{17} Z imidazole (4)	0.2	0.2	0.2	0.2	0.2	0.2
Modaflow 2000 (5)	0.5	0.5	0.5	0.5	0.5	0.5
Benzoin	0.5	0.5	0.5	0.5	0.5	0.5
TiO_2	43.0	43.0	43.0	43.0	43.0	43.0

(1) Reichhold Chemicals, Inc.
(2) DuPont Plastics
(3) Dibutyl Tin Dilaurate- Synthron, Inc.
(4) Air Products, Inc.
(5) Monsanto, Inc.

PROCESSING NOTES

PREMIX: Each batch blended in Henschel mixer for 30 seconds @ 2000 RPM.
EXTRUSION: Werner & Pfleiderer ZSK-30 twin-screw extruder:
250 RPM screw speed
Feed rate = 60 lbs./hr., Barrel temperatures: Zone 1 = 90 ^{0} C, Zone 2 = 80 ^{0} C.
Extrudate passed through Strand chill rolls and ground using a Brinkmann ZM-1 centrifugal mill @ 15,000 RPM. Powder classified through a U.S. 200 mesh screen (75 microns) and sprayed onto cold rolled steel with a Nordson Versa-Spray electrostatic spray gun.

TABLE 5 :**Acrylic/Polyester Powder Coating Evaluations: MATTE TO HIGH GLOSS**

Formulas I-VI: Bifunctional Polyester/GMA Acrylic/ IPDI

Formula No.	I	II	III	IV	V	VI
Baking Schedule, min./°F	10/400°F	10/400°F	10/400°F	10/400°F	10/400°F	10/400°F
Film Thickness,mils	2.5 mils	2.3 mils	2.0 mils	2.6 mils	2.0 mils	2.0 mils
Gloss,60°/20°	**10/2**	**25/3**	**40/8**	**55/13**	**70/22**	86/42
"b" value	0.7	2.3	1.7	3.0	1.0	2.9
PCI Flow Rating (1-10)	6	4	4	4	5	5
Pencil Hardness	H	H	H	H	H	H
Gardner Impact:F/R (5/8"), IN.-LBS.	160/160	160/160	160/160	160/160	100/100	100/40
Mar Resistance	good	good	good	good	good	good
Crosshatch Adhesion	100%	100%	100%	100%	100%	100%
Solvent Cure Test (PCI # 8 B)	full cure	full cure	part.cure	part.cure	part.cure	part.cure
Inclined Plate Flow (PCI # 7), mm	40 mm	51 mm	56 mm	54 mm	59 mm	59 mm
Gel time (PCI #6), seconds	30-40 sec.	35-40 sec.	35-40 sec.	45-50 sec.	45-50 sec.	45-50 sec.
100 % Overbake Resist., Gloss 60°/20°	10/2	24/4	40/5	56/12	67/22	85/46
100 % Overbake Resist., "b" value	0.9	2.75	2.1	3.5	1.9	3.3
Delta b	0.2	0.45	0.4	0.5	0.9	0.4

TABLE 6:Matte to High Gloss Acrylic/Polyester Powder Coatings

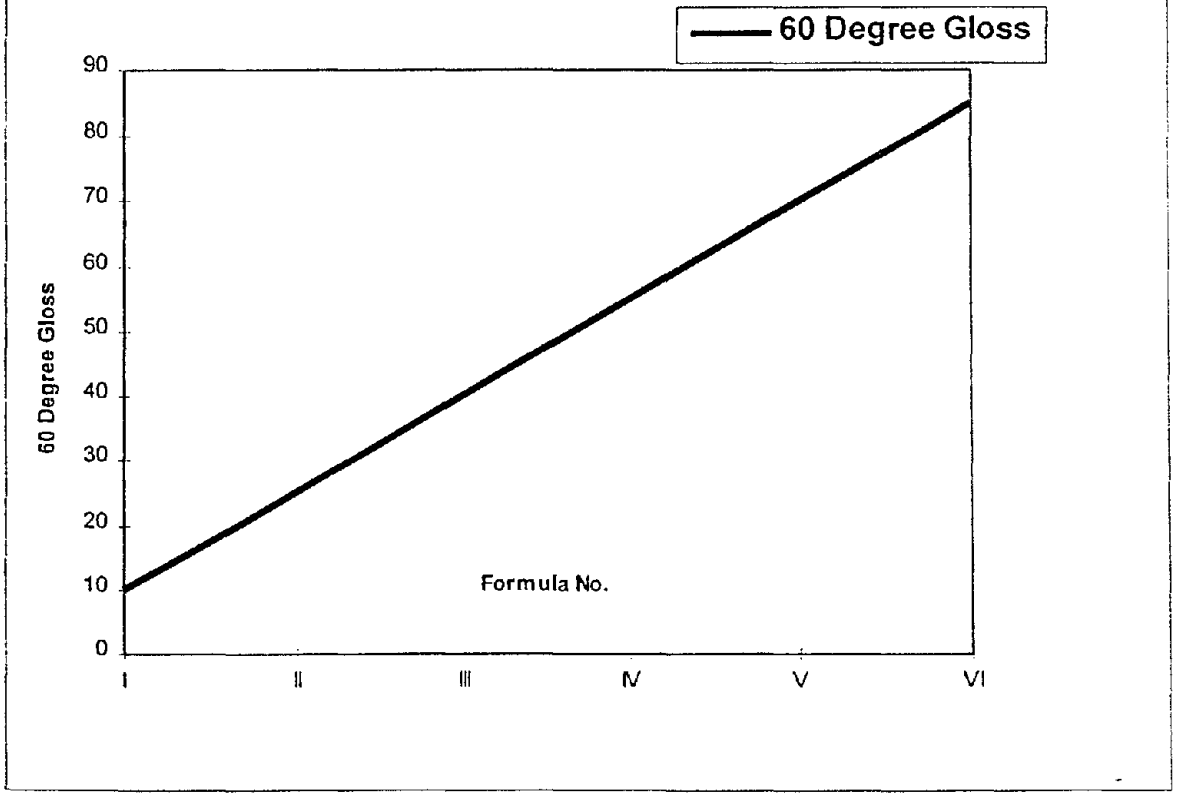

TABLE 7

TIME/TEMPERATURE CURE MATRIX FOR MATTE FINISH:
(FORMULATION I,TABLE 4)

	60^{0} GLOSS
10 MINUTES @ 180 ^{O} C	9.1
20 MINUTES @ 180 ^{O} C	8.0
30 MINUTES @ 180 ^{0} C	7.5
10 MINUTES @ 200 ^{0} C	8.6
20 MINUTES @ 200 ^{0} C	8.1
30 MINUTES @ 200 ^{0} C	9.5

SESSION 7A

AUTOMOTIVE APPLICATIONS

PAPERS PRESENTED:

"Reduction of VOC Emissions from Painting of Car Bodies - a Case Study of Two Swedish Car Plants"
by
Peter Adler
Swedish Environmental Protection Agency
Stockholm, Sweden

"New Low VOC Fluorinated Coatings"
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Massimo Scicchitano
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"Supercritical Fluid (SCF) Adhesion Promoters for Automotive Plastic Applications"
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Reductions of VOC emissions from painting of car bodies - a case study of two Swedish car plants

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INTRODUCTION

The two major Swedish car plants constitute significant point sources of VOC emissions in a part of the country which is subject to high total VOC emission levels. The plants have received conditions according to the Environmental Protection Act stipulating that their emissions of volatile organic compounds should be gradually reduced until they reach a level of approximately 2 kg of VOC per car body. According to the conditions, this final goal should be reached by 1998 or 2000.

Emissions have already decreased significantly. The companies' efforts to reduce emissions are carried out with insight from, and in consultation with, the environmental authorities at local, regional and national level.

In this paper, the conditions in the two factories permits are presented, followed by information on past and present VOC-emissions. After this a general technical description of implemented and planned abatement measures for different processes is given, with emission factors (kg VOC/car) for each process.

VOLVO, TORSLANDA[1]

Conditions in the permit

Emissions of VOCs may not exceed the following values:

1992 - 1995	1 100 tons per year
1996 - 1997	700 tons per year
from 1998 inclusive	450 tons per year

The emission limits include all emissions from the whole factory, but they are not related to the degree of capacity utilization. The permit allows for the production of 260 000

car bodies per year and the assembly of 170 000 cars per year. However, the actual highest production of car bodies is not likely to exceed approximately 200 000 per year.

The paint shop for small parts may paint 235 000 detail racks per year, and the spare parts paint shop (electrodip) may paint 1 500 000 m^2 per year. Emissions from certain activities which cannot be directly related to the production of cars, such as painting of trucks, and laboratory and development center, are also included in the emission limit.

VOC emissions past and present

VOC emissions were approximately 23 kg/car body before work was started during the 70'ies in order to reduce them.

In 1989, when the old paintshop was still in full use, VOC emissions from the whole plant were 1794 tons, of which 1750 tons can be more or less related to the production of cars; that year 178 000 car bodies were painted and 134 000 cars assembled. In 1994, with the old paintshop virtually discontinued, emissions related to the production of cars were according to preliminary figures 350 tons (approx 105 000 car bodies painted, 94 000 cars assembled). Emissions were thus an average of 3.3 kg/produced car, or 2.7 kg/car body if the 71 tons from the small parts paint shop are excluded.

Electrodip

The consumption of solvents in the electrodip paint shop is approximately 0,82 kg/car body. Of this, about 20% is incinerated in the afterburners on the drying ovens, and about 50% leaves the paint shop in waste water. The solvents in question are biodegradable, and calculations have shown that they will mostly not evaporate before reaching the public wastewater treatment plant.

Lead-free electrodip that has been introduced in the spare parts paint shop contains a third as much solvent as the ordinary electrodip. Volvo plans to introduce the lead-free paint for electrodipping of car bodies as well, but there are still technical problems left to solve.

The new paint shop for surfacer and topcoat

The new paint shop, with far-reaching abatement measures, started production in the autumn of 1990 and has, after a fairly long period for starting up, since the middle of 1993 painted virtually all the car bodies which are painted at Torslanda.

In 1994 the emissions from the new paint shop were (104 000 car bodies painted):

Source	*Emission (tons)*	*Emission (kg/car body)*
Abrasive resistant paint etc	8.7	0.08
Surfacer	12.4	0.12
Basecoat	87	0.84
Clearcoat	22.4	0.22
Cleaning of painting equipment and booths	31	0.30
TOTAL	161	1.55

Waterborne paints. Virtually all basecoats are waterborne, typically with 13 - 15% solvents. The metallic basecoats have a rather low content of paint solids, generally 15 - 25%.

Destruction of solvents. Air from the application of abrasive resistant paint, surfacer and clearcoat is concentrated with respect to solvents. Air from automated spray booths is recirculated over the booths, whereas air from manual application of surfacer and clearcoat is concentrated in active carbon filters. The concentrated air flows are incinerated in regenerative sand beds. Air from the storage tanks for paint booth scrubber water is ducted back to the paint booth, so this air is also cleaned.

Solvents in ventilated air from paint-mixing rooms, and air from sedimentation tanks for scrubber water from solventborne booths, are concentrated in a zeolite rotor and then ducted to the same incineration equipment as the solvents from painting.

Flue gases from all drying ovens are treated by incineration.

Cleaning of equipment and booths. Booth walls and some equipment are coated with a substance that enables paint to be removed using high pressure water. Booth windows and other equipment are coated with a plastic film, so that paint can easily be removed by removing the film.

Non-fixed spraying equipment from both solventborne and waterborne booths is cleaned in special rooms. The air from

these rooms is ducted to the same abatement equipment as air from the paint-mixing rooms.

Such solvents that still need to be used for cleaning of booths and equipment (*eg* equipment that cannot be treated with protective layers as described above) in solvent-borne booths are collected and sent to be distilled at an external plant, for reuse at Volvo.

The remaining emissions of VOCs from cleaning come mostly from in-booth cleaning of equipment for waterborne paint. The solvents used for this consist mostly of butyl glycol.

Emission figures for solvents from cleaning are calculated as 10% of the net consumption (*ie* excluding solvents recollected for redistillation) in booths connected to abatement equipment, and total net consumption in booths that are not connected to abatement equipment.

In the "bad old days" there was much less check of how much solvents were used, but consumption is estimated by Volvo to have been up to 1 500 tons per year. Collection of solvents for redistillation was started in 1986/1987; before then all cleaning solvents were emitted. Nowadays, much greater care is placed on not using more cleaning solvents than necessary. The economizing on solvents for cleaning has been good for the external environment, for the workplace environment, and for finances.

Efficient application of paint. The amount of overspray is reduced by using electrostatic equipment. Virtually all layers covering the complete outer surface are applied using electrostatic bells, with only 10 - 15% overspray. Handguns have also been improved in order to reduce overspray from manual application. However, Volvo is gradually going over to automated application on the inside of bodies as well. This should increase transfer efficiency, perhaps from about 30% to 40%, thereby decreasing paint consumption in proportion.

Underbody coating

Volvo has gone over to underbody coating that is of the hot-melt kind, with no solvents, using heat instead to get sufficiently low viscosity for application. This is applied after topcoat. Before, VOC emissions from underbody coating were 4.7 kg/car. The 0.23 kg/car that are still emitted come from the coating of chassi details which are fitted during assembly.

Cavity protection material

The dry content in cavity protection material has been increased to 64%, and the quantity that is applied has been optimized, so that resulting emissions (=consumption) of solvents are down to an average of 0.16 kg/car.

The aim is to go over to 100% solids material. (This has already been achieved at Volvo's equivalent plant in Flanders.)

Assembly and final adjustment

Emissions of solvents from assembly and final adjustment are approximately 0.25 kg/car. Use of solvents for cleaning equipment and workplaces has been dramatically reduced by introducing formalized routines for the issuing of solvents to personnel. Water-based cleaners have largely been able to replace solvents.

Repair painting of originally waterborne coats is done with waterbased paint.

Volvo has started to use "wrap-guard", a plastic paint-protection film, that is put on already after the car-body paint shop and stays on throughout assembly. This has meant that the amount of repair painting has decreased. This also serves as paint protection for delivery, thereby more or less eliminating the use of other paint protection.

Nowadays, the only fluid paint protection that needs to be applied is in the engine compartment, and waterborne material is used as long as there is no risk for frost.

Small parts paint shop

Measures against VOC-emissions from the small parts paint shop, which paints small parts for cars produced both at the Torslanda plant and at Volvo's plant in Flanders, can basically be the same as from the main car body paint shop. However, due to the fact that the present small parts paint shop is not designed for waterborne paints, and to some other technical problems, abatement has not come as far. Emissions from this paint shop thus were as much as 71 tons in 1994, but measures to decrease emissions are planned.

Conclusions

Leaving aside the small parts paint shop, results already reached or expected in the near future at the Torslanda plant should give the following emissions from activities related to the production of cars: electrodip 0.1; abrasive resistant

paint to clearcoat 1.3 - 1.5; underbody coating 0.23; cavity protection material ~0; assembly and final adjustment 0.25; paint protection ~0; altogether approximately 2 kg/car.

SAAB AUTOMOBILE AB, TROLLHÄTTAN[2]
Conditions in the permit

Emissions of VOCs to air are not allowed to exceed the higher of following values A or B for each year; nor are emissions allowed to exceed the values C:

	A tons per year	B kg/car, yearly average	C tons per year
1995 - 1996	550	7.0	840
1997	275	6.0	700
1998	275	4.5	525
1999	275	4.5	460
from 2000 inclusive	275	-	-

The permit allows for the production of 120 000 cars per year.

VOC emissions past and present

VOC emissions were approximately 20 kg/car body up to the beginning of the 80'ies, when work was started in order to reduce them.

Below, emissions expressed in kg/car are compared for 1990 (when 57 000 cars were produced) with planned emissions for 1994 and 2000.

Source	*emission in kg/car*		
	1990	*1994*	*2000*
Primer	0.93	-	-
Electrodeposition	1.2	0.06[3)]	0.06[3)]
Surfacer and under-body coating	2.4	0.85	0.18
Topcoat	4.8[2)]	4.4	0.92
Cavity protection material	2.0[2)]	0.05	0.05
Assembly, final adjustment and paint protection	0.70	0.10	0.10

Cleaning[1] and miscellaneous	1.5[2]	1.7	1.0
TOTAL	13.4	7.1	2.3

[1]Emissions from cleaning do not include solvents that are collected and redistilled.

[2]Emissions that in 1990 were reported from the major paint shops probably include certain emissions from cleaning, that in later years have been reported as such in order to get a better grip of how large emissions from cleaning are. This does not change the figure for total emissions.

[3]Emissions from the new electrodip might be 0 to 0.2 kg/car higher if emissions of solvents to water are emitted to air at a later stage.

Electrodip and primer

The anodic electrodeposition (on the inside of the body) and the primer (on the outside), which together emitted approximately 2 kg VOC per car, were replaced in spring 1993 with a cathodic electrodip. The flue gases from the drying oven are incinerated in an afterburner. The ventilation from the application of the paint is ducted to the drying oven and thence to the afterburner; the energy cost for the further emission reduction thus achieved is approximately 1 USD per kg VOC.

Underbody coating

The dry content in underbody coating has been increased to 83 % dry content by weight; suitable viscosity for application is achieved by heating to 50°C. Including the effect of the drying oven's afterburner, which is estimated to incinerate 90% of VOCs in the underbody coating, resulting emissions from underbody coating are estimated to be 0.12 kg/car. (Measurements at SAAB have shown that virtually no solvents are emitted from the underbody coating during application.)

Surfacer and topcoat

Continuous improvement. Emissions have already been reduced through increased concentration of dry substance in metallic paint and other paints, electrostatic application with rotating bells, and optimization of surface thickness and of application area.

Overspray. The VOC emissions resulting from overspray are significant - despite improvements they are still about 1 kg/car body from solid topcoat and 2 kg/car body from metallic basecoat with clearcoat. Overspray is approximately 25 - 30% from automated spraying, but a lot higher from hand-spraying. Hand-spraying is used for the inside of car bodies and for the final coat on the outside of metallic paints.

Planned new paint shops in the 90's. The present surfacer is planned to be replaced by a waterborne surfacer. Waterborne surfacers with a solvent content of 3-4% are available on the market. Powder-coat surfacer might also be a possibility, with interesting developments in that area going on in the USA.

The present system for topcoat - a single paint layer for solid colors and a basecoat layer and a clearcoat layer for metallic colors - will be replaced with a system with both basecoat and clearcoat irrespective of color type. The basecoat is planned to be be waterborne. Either the clearcoat will be waterborne or the flue gases will be cleaned from solvents. The intermediate drying zone between basecoat and clearcoat is planned to be ducted to a drying oven's afterburner. Altogether, VOC emissions from topcoat will be reduced to about 1 kg/car, compared with about 6 kg/car (metallic) and about 3 kg/car (solid) in 1992.

Cleaning of equipment and booths

Protective polyethylene films are applied on paint-spraying equipment and on paint booth windows. The films can be removed by hand when paint has built up on them, and deposited as fairly harmless waste. A water-soluble resin is applied to paint booth walls, so that they can be cleaned using high-pressure water. In these ways, cleaning solvents are avoided.

Use of water/butylglycol mixtures replace organic solvents for the cleaning of equipment where waterborne paint is used.

Use of teflon-coated gratings in the spraybooths in order to decrease the building up of paint on these surfaces is being discussed.

A number of different measures, such as reducing the number of locations where cleaning with solvents can be carried out, and adding lids to cleaning trays, have improved housekeeping of solvents.

Thinners used for cleaning the paint distribution system is collected (and distilled in-house for reuse).

Cleaning is still a significant source of VOC emissions, but they come from many small-scale sources, rather than from a large easily identified process, and are thus easily overlooked. The size of the emissions is also very much the result of how careful individuals are when cleaning equipment. SAAB has for these reasons striven to increase awareness on the shop floor of how important carefulness in cleaning is for reducing the factory's environmental impact.

Cavity protection

The dry content in cavity protection material has gradually been increased. Many years ago, VOC emissions from such material ran to many hundreds of tons per year. In 1991, emissions had been reduced to approximately 1.3 kg/car. Cavity protection material consisting of >99% solids has now been introduced, giving emissions of approximately 0.02 kg/car, and lower costs. This also improves the working environment, through decreased evaporation of VOCs from car bodies on production lines after the cavity protection treatment. Furthermore, spillage of cavity protection material on car bodies and equipment can now be removed using detergents instead of solvents.

Assembly

Solvent-based corrosion protection materials applied during assembly are gradually being substituted by other protection on parts, *eg* hot dip galvanizing.

Parts of car bodies that are easily damaged are covered with protective plastic shields during assembly, thus decreasing the need for repair painting.

Afterburners

Installation of afterburners after drying ovens for surfacer and underbody coating, for metallic and for corrosion protection have decreased emissions by 1.9 kg/car.

With the planned new paint shops, all drying ovens will have afterburners.

Paint protection

Previously, solventborne material was used for temporary paint protection treatment, but SAAB has now switched over to waterborne material. This has decreased emissions from about 0.6 kg per treated car to virtually nil (0,01 kg/car). This also leads to reduced VOC emissions when the paint protection is removed: solventborne material will generally be removed

using petroleum spirits, wheras waterborne material can be removed by aqueos cleaners (that do, however, contain EDTA).

Paint sludge

Analyses carried out on SAAB's paint sludge from topcoat (solventborne) showed that the VOC content is 3 - 7%. However, most of the VOC that was in the sludge consisted of butanol, which was shown in another experiment to evaporate from the sludge more slowly than the water did.

Sludge from topcoat (approximately 150 - 200 tons in 1993) is at present incinerated in a municipal solid waste incinerator; this seems to be working well, but a final decision on whether to continue with this arrangement on a regular basis has not yet been taken. The solvents that are destroyed in this way have not been deducted from the emission figures quoted above.

Conclusion

The sum of VOC emissions from electrodeposition, underbody coating, surfacer, basecoat and clearcoat will thus be approximately 1.2 kg/car. Emissions from cavity protection material and assembly etc are now less than 0.2 kg/car. Together with planned decreases in emissions from cleaning, total emissions should be down to 2.3 kg/car by the year 2000. With the possible exception of end-of-pipe abatement after clearcoat if solvent-borne is chosen, this decrease will have been achieved solely by good housekeeping and using low-solvent materials.

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NEW LOW V.O.C. FLUORINATED COATINGS

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INTRODUCTION

A well known problem in the manifacturing industry is the aspect related to the coating operations on finished or semi-finished articles. Coatings are applied to protect the substrate and improve the aspect. The process frequently involves the use of solvents as film forming coadiuvant and diluent; the solvent release into the atmosphere is the source of one the major concerns of the manifacturing industry. The future regulations and laws claim for the reduction of Volatile Organic Compounds (VOC) to obtain environmental friendly coatings. According to this view, paint producers are working in two directions: the former towards formulations having a lower solvent amount, the latter to develop technologies characterized "per se" by low V.O.C. Thus, water based and powder coatings are increasingly used, although this approach hardly meets the requirement of the market in terms of quality and durability of the final material.

A really innovative system should present the following profile:

- to match the most restrictive coming laws concerning the problem of solvent emission into the atmosphere
- to be applicable with the existing apparatus
- to be a high performance material: durability, protection, appearance.

Fluoropolymers as starting materials for high performance coatings are well known expecially for their superior durability, weatherability and chemical resistance[1]. Polyvinylidene fluoride[2] (PVDF) is widely used in the architectural field; it is a high molecular weight thermoplastic fluoropolymer which is usually formulated with acrylic resins in a latent solvent paint to improve the rheological behaviour and adhesion. PVDF coatings are considered as particularly suitable for long term outdoor expositions.

More recently, thermocurable fluoropolymers[3] were developed consisting of chlorotrifluoroethylene/vinylethers or vinylesters alternated copolymers with free OH pendant groups. In any case, the relatively high molecular weight of these polymers (>10000) and the intrinsic stiffness of the main chain cause a high viscosity and, consequently, a large amount of solvents is required for a correct application. Therefore, these formulations have a solid content around 10 - 40 %, and that fact appears as a serious drawback and limitation in a future wider use of these coatings.

Perfluoropolyethers (PFPE) and their functionalized derivatives present , on the contrary, an exceptionally high

chain flexibility and a molecular weight easily available in the oligomeric range[4]. Their resistance to aggressive environments (chemical, thermal, photooxidative) is excellent[5], and their bulk viscosity is generally low enough to require a very reduced amount of solvent in formulation: in principle, fluoropolyether derivatives offer the possibility to join a low V.O.C with high performances characteristic of fluorinated coatings.

THE RESINS

In this work, hydroxy bearing resins will be described as useful for one-pack coating formulations. The table 1 reports the main features of this new class of fluoropolyether based resins, named FLUOROBASE Z (FBZ). They consist of a random perfluoropolyether chain $(CF_2CF_2O)_p(CF_2O)_q$- having primary and secondary hydroxy functions; a minor number of -COOH groups can be optionally present. The molecular weight is tipically comprised between 1000 and 2000. The composition of the PFPE chain determines a p/q ratio generally close to 1: the quite random distribution of the $-CF_2CF_2O-$ and $-CF_2O-$ units prevents any possibility of crystallization and the fluoroetheric nature imparts the characteristic flexibility, evidenced by the low Tg value. The whole macromolecule consists of C-C, C-O and C-F simple bonds and the hydroxylic functionality (that is the number of reactive groups per molecule) is 2 - 4.

Table 1: Main features of new FLUOROBASE Z resins

Resins type	FBZ 1010	FBZ 1020	FBZ 1030	FBZ 1040
OH functionality	2.8-3.0	3.8-4.0	1.9-2.2	3.3-3.6
Acid Number	-	-	-	10-25
Viscosity(cP,20°C)	300-600	2500-3000	80-150	5000-6000
Glass Transition(°C)	-90/-100	-80/-90	-100/-110	-60/-70

The viscosity (data given at 20° in table 1) ranges from 100 to 6000 cP mainly depending on functionality, with a minor effect of the flexible chain.

Viscosity of these resins is strongly influenced by addition of few percents of solvent: the figure 1 shows the viscosity-concentration dependence of FBZ 1030 in three different solvents (a fluoroalkane, a ketone, an alcohol), whereas the figure 2 shows the viscosity-

concentration curves (on a semilogarithmic plot) of FBZ 1010, 1020 and 1030 in methyl isobutylketone (MIBK). It appears that fluoroalkanes ("good" solvents of PFPE chain[6]) have a much lower effect on the resin viscosity with respect to ketones and alcohols which are "poor" solvents of PFPE. Furthermore, the viscosity reducing power of polar solvents is more marked for higher functionality resins (FBZ 1020). All these experimental evidences suggest that viscosity of these PFPE based polyols is dominated by polar interactions (as hydrogen bonds) among the ends which create intermolecular associations.

A very limited amount of a polar solvent enables to reduce steeply viscosity of the mixture disrupting these associations, while fluorinated non-polar solvents cannot compete with hydrogen bonds, so showing a lower

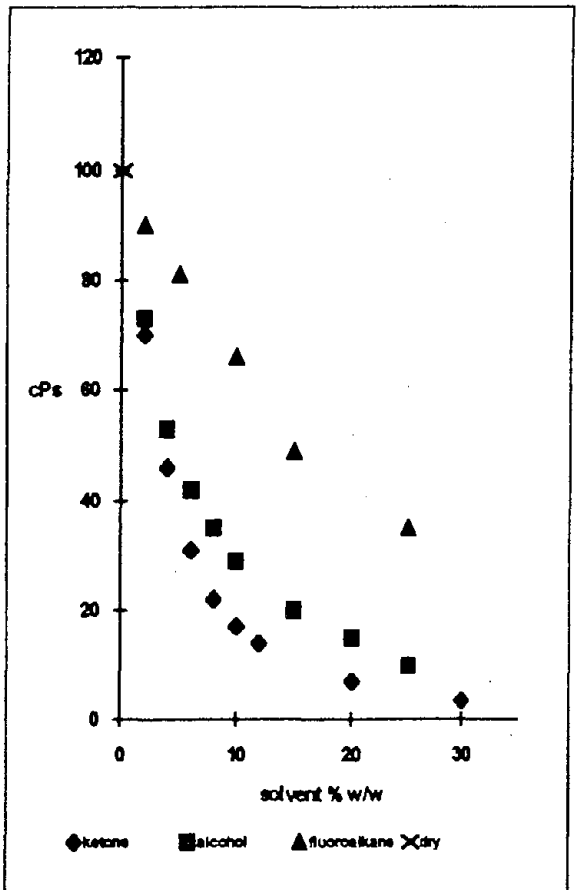

Figure 1: Viscosity of FBZ 1030 in various solvents at T = 25°C.

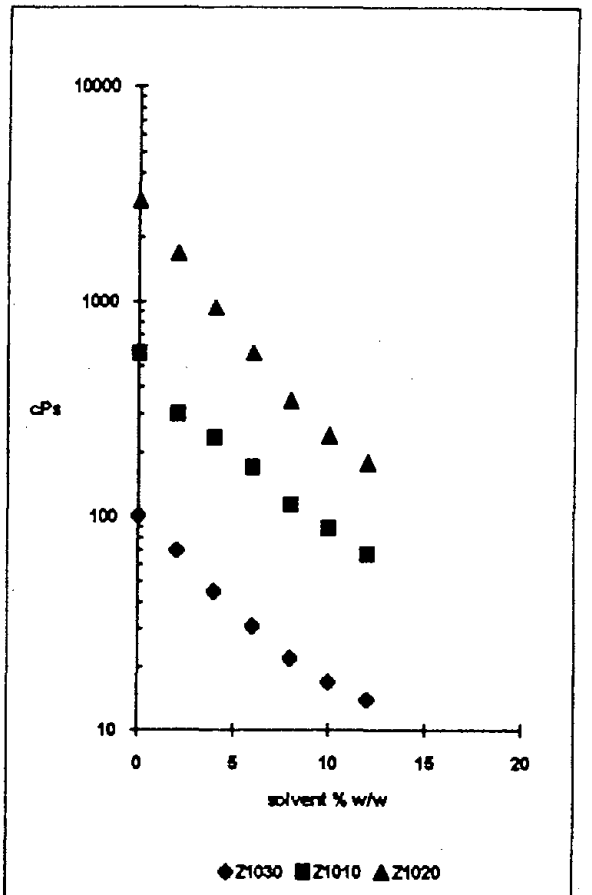

Figure 2: Viscosity of FBZ resins in MIBK at T= 25°C.

viscosity reducing power. Similar effects were described[7] also concerning other polyolic "hydrogenated" resins (acrylics), but the viscosity reduction caused by polar solvents on FLUOROBASE Z resins is more marked due to

the high selectivity of the end group solvatation and high molecular mobility of the PFPE chain.

It should be noticed that alcohols, esters, ketones are very useful solvents for one-pack coating formulations; these fluoropolyether based resins can be considered as structurally suitable for the preparation of new high-performance low VOC coatings, in that generally few percents of a proper solvent are enough to control the rheology of the system to the specific applicative need.

THE FORMULATIONS

FLUOROBASE Z resins can be formulated with a variety of common melaminic and isocyanic hardeners; typical examples are monomeric and oligomeric methylated melamines (commercial CYMEL 303 and 325) and ketoxime-blocked IPDI and HDI isocyanurates (VESTANAT B1358 and DESMODUR BL3175 respectively). Solvents suitable are butanol, butyl acetate, PMA, MIBK and others belonging to the same classes. At the same time, curing conditions are conventional: 140-150 °C./30 min with p-toluensulfonic acid catalysis for melamines, 150-180 °C./30-10 min with dibutyl tin dilaurate catalysis for blocked isocyanates. The resin FBZ 1040 is preferred in melamine based formulations because its higher acid number makes easier compatibilization (even without solvent) and catalyzes the crosslinking reaction. Compatibility (meant as the possibility to obtain clear formulations of FBZ resins), is generally good with ketoxime blocked polyisocyanates and it seems easier for the lower functionality resins (FBZ 1010 and 1030). Due to its high OH functionality,it is advisable using alcohols as butanol in formulations based on FBZ 1020; in any case , aliphatic or aromatic hydrocarbons should be eliminated previously if present in the commercial hardener (for ex. BL3175).

The solid content achievable is 100 - 80% for melamine formulations and 85 - 70 % for the higher viscosity blocked isocyanurates. Also taking into account the evaporation of the blocking agent (methanol and methyl ethyl ketoxime), interestingly low VOC coatings are obtained.

It should be noticed that solvent is used exclusively for reducing the viscosity of the formulation, while good coating appearance and correct film formation are assured by the flexibility and the newtonian behaviour of the PFPE chain also without solvent.

The knowledge of viscosity - temperature dependence of these formulations can be of concern in view of particular technologies (as hot spraying, for example) allowing to reach the best results in terms of low VOC. Thus, the figure 3 shows the viscosity-temperature relation for some formulations according to an Arrhenius type plot. It seems that an approximated straight line dependence is

followed, likely thanks the low Tg value[7] and the good compatibility of the fluoropolyether resins with the hardeners. That fact assures the possibility to foresee easily the effect of temperature on viscosity which is, around 50°C, generally comprised between 50 and 500 cP.

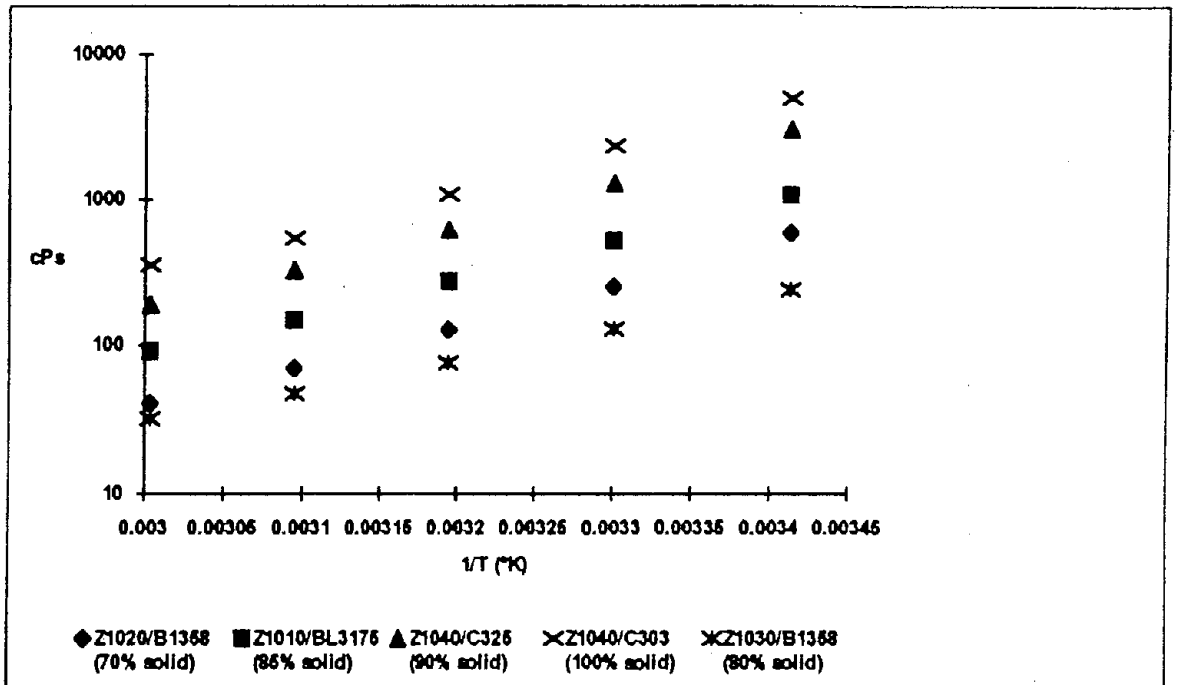

Figure 3: Viscosity-temperature relation of FBZ formulations.

THE COATINGS

As a general rule, the polyurethanic materials previously described always show two distinct Tg values. The former glass transition temperature is generally located around -100°C and corresponds to the fluoroetheric segregated phase. The Cp variation at the transition is rather low (about 0.01 cal/g) and the Tg is sometimes difficult to evaluate, especially for FBZ 1020 cured films where the weight fraction of fluorinated moiety is lower. The latter thermal transition should be attributed to the urethanic "hydrogenated" phase; significant differences may be observed moving from the HDI cured films to the IPDI ones and, within each class, changing the hydroxy functionality of the resin. In fact, the degree of crosslinking appears as a factor regularly influencing the upper Tg value, which varies from about -10° to +30 °C. (HDI cured) and from +65° to +145 °C. (IPDI cured), in both cases changing the OH functionality of the resin from 2 to 4.

The melamine cured films show, on the contrary, a only Tg value at about 160 °C. without other detectable transitions at lower temperatures. The lack of the "fluorinated Tg" may be partially due to a relatively low sensitivity of the DSC method and partially to a real constraint effect exerted on the PFPE chain by the highly crosslinked polymeric network which strongly lowers its degrees of freedom.

The typical two-phases morphology of the fluoropolyether polyurethanes finds a close correspondence also in their mechanical properties. Stress-strain curves[8] were carried out at +23°C on self-supported films peeled off PTFE or PFA plates after curing. As an example, the figure 4 shows the comparison between the tensile curves of FBZ 1030 films cured with BL3175 and B1358.

The presence of a glassy phase (Tg +65°) in the latter material determines a tough-plastic behaviour with yielding occurring around 30-35 MPa (yield stress) and 6-7% (yield strain). The HDI cured film is, by contrast, tested at a temperature above any thermal transition and it shows a rubberlike behaviour with no yielding phenomena and much lower tensile strenght than in the former case. The rupture strain (about 80%), noticeable for a coating, is practically the same for both cases in that it is determined mainly by the chain lenght of the soft segment (the PFPE chain) among the chemical junctions of the polymeric network . Analogous considerations could be done also for the FBZ 1010 and FBZ 1020 coatings taking into account a progressive increase in tensile strenght and decrease of rupture strain regularly increasing the OH functionality of the resin.

For all these evidences it can be argued that IPDI based hardeners are surely more appropriate in order to obtain coatings characterized by mechanical properties (i.e.

hardness) of interest for the high temperature applications. In any case, the presence of a relevant rubbery segregated phase imparts a noticeable flexibility to these polyurethanic coatings (the T-bend test performed on coated aluminum panels is tipically 0-1 T), which could be very useful especially for the coil-coating technology .

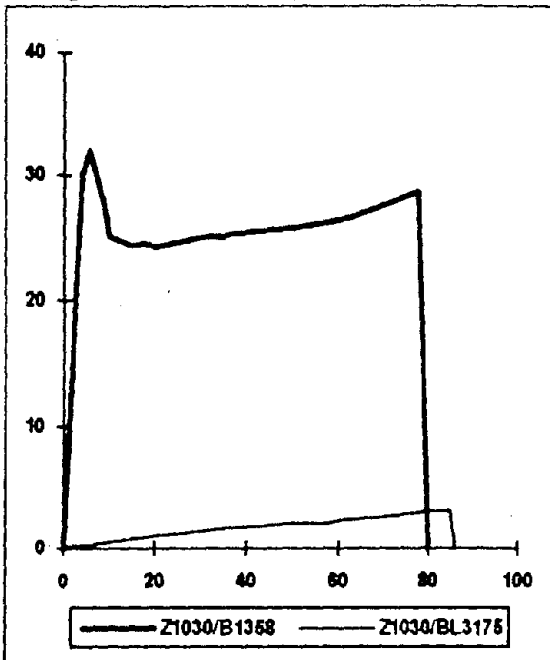

Figure 4: Stress-strain curves of the crosslinked films

An important consideration should be done about the appearance of these new materials. In spite of the presence of generally well segregated phases, all these coatings appear as quite transparent without any haze effect (transmitted light through coated glass panels is always 100%). This may be explained invoking the presence of microdomains sized exclusively well below the wavelenght of light. That fact is very important because it allows the use of these materials as clear coats without loosing some relevant properties inferred by the multiphasicity, like the good flexibility and formability.

Melamine cured films are also characterized by a complete transparency: the application conditions, the good adhesion on various primed substrates and the high fluorine content make these coatings as promising high protection topcoats in the automotive technology. Solvent-less coatings can be reached using these new fluoropolyether based resins. An example is given by FBZ 1040/CYMEL 303 coating (hardener 20-25% w/w), which components are completely miscible even without solvent; the viscosity (around 5000-6000 cP at ambient temperature) can be furtherly reduced by hot applications or, eventually, studying CO2 based systems. The leveling of such a coating is very high notwthstanding the absence of a solvent.

The table 2 summarizes some relevant properties of melamine cured FBZ coatings. The values of hardness and gloss are acceptable notwithstanding the high content of "soft" and low refraction index perfluoropolyether. On the other hand, the very high fluorine content determines a high inertness to chemicals as acids and organic solvents, and an exceptionally high abrasion resistance (evaluated as gloss retention after a standard mar test used in the automotive

industry). These outstanding performances are surely related to the low coefficient of friction and reduced contact area typical of highly fluorinated materials. Accelerated weathering tests on the films are in progress, even if previous experiences carried out on fluorinated resins have stressed out an exceptionally inertness even in very drastic conditions (U.V. radiation, chemicals, humidity); this is a fundamental starting point to obtain coatings showing very high weatherability.

Table 2: Properties of melamine cured FBZ 1040 films

VOC (ASTM D 3960-81)	180-400 g/L (1.5-3.3 Lb/Gal)
Fluorine Content	32-36% w/w
Hardness (Persoz)	230-250
Gloss (60°C)	78-85
D.O.I.	excellent
Conic Mandrel	< 3.17
Abrasion Resistence (Gloss retention)	95-98 %
Acid Resistance (Spot Test, H_2SO_4 38%, 25°C)	no effect
Solvent Resistence (Spot Test, MEK, Xylene, 25°C)	no effect
Adhesion (Cross cut test, on primed panels)	100 %

CONCLUSIONS

Fluoropolyetheric polyols can be considered as the most suitable resins in order to obtain low VOC and high performance coatings. In fact, the hydroxy functionality imparts crosslinkability and promotes compatibility with solvents and hardeners through polar interactions. On the other hand, the oligomeric PFPE chain gives a very limited contribution to viscosity and, furtherly, assists the correct film formation during the curing process thanks its high flowability. The bulk viscosity of the resin may be tuned to the desired value by hot application or addition of limited amounts of solvent, which selectively interacts with polar end groups. Low VOC coatings are therefore available for the high temperature technology (coil-coating, automotive, architectural) characterized by good resistance towards abrasion and chemicals. Further studies are developing in order to set up also low temperature curing low VOC fluoropolyether based coatings.

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SUPERCRITICAL FLUID (SCF) ADHESION PROMOTERS for Automotive Plastic Applications

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INTRODUCTION

The growth of thermoplastic polyolefins (TPO) for the automotive plastics market is pushing industry to better understand issues regarding the application of coatings to TPO substrates. Some of the issues relate to federal, state and county environmental regulations; adhesion and penetration of the coating into the substrate as well as the intercoat adhesion between layers of coatings. One method of resolving some of these issues is using chlorinated polyolefins (CPO) tie-coats to assist in the adhesion of topcoats to untreated TPO.

An alternative spray process, the supercritical fluid (SCF) process was developed for applying solvent borne (CPO) adhesion promoters to TPO. This paper will discuss how during plant trials, the SCF process dramatically reduced solvent emissions, improved application efficiency, and enhanced product performance.

ADHESION PROMOTERS

Adhesion promoters are coatings specifically designed to promote adhesion to hard-to-adhere-to substrates like thermoplastic olefins (TPO). Adhesion promoters are typically non-reactive, one component (1K) solvent-borne polymers, averaging less than 10% volume solids. The products are normally HVLP applied at 0.2 to 0.4 mils dry film thickness. Adhesion promoters use chlorinated polyolefin resins (CPO) to obtain adhesion to TPO and modifying resins to acquire adhesion of a polyurethane topcoat to the primer. Optimization of these resins is key to assuring peak performance. Adhesion promoters are primarily composed of aromatic solvents because CPO resins are best solubilized and most stable with aromatics. Because TPO consists primarily of polypropylene, and is a difficult substrate for standard polyurethane coatings to adhere to, it is necessary to use an adhesion promoter.

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There are also other pretreatments available for TPO which eliminate the need for an adhesion promoter; such as vapor degreasing, UV light irradiation (utilizing Benzophenone), flame treatment, gas plasma, and corona discharge. But due to environmental regulations and cost, these methods have not been widely used in North America.

By far, the easiest method for reducing VOC of the adhesion promoter would presumably be reducing its solvent content and increasing its solids content . This, however, is much more difficult then it appears. The key component in adhesion promoters, the CPO resin, requires a substantial amount of solvent to bring it to a sprayable viscosity. Solvent contents of 6.5 to 7.0 lbs. per gallon are normally required for proper spraying and leveling of the wet film.(1) Reductions in solvent content give high viscosities and poor atomization which causes spotty application with significant orange peel. The film does not sufficiently wet the substrate surface and also causes minimal adhesion. The high degree of orange peel can profile through the topcoat, resulting in an unsatisfactory painted surface with lower DOI.

For these reasons an alternative spray process, the supercritical fluid (SCF) spray process was tested because it could spray a higher viscosity product, and reduce the VOCs. The process could also produce a satisfactory film with good atomization, flow, and leveling properties.

SUPERCRITICAL FLUID (SCF) SPRAY PROCESS APPROACH

The supercritical fluid spray process for the application of coatings was first proposed in 1990 as a new pollution prevention technology. (2) The process uses carbon dioxide to replace the volatile organic solvents used in conventional and high solids coating formulations. The technical developments of the process were described in 1993. (3-4) Early results showed that the process could actually improve coating appearance, improve corrosion resistance and performance when removing most of the solvent from solvent-borne formulations. (5) The polymer chemistry and phase relationships of coating concentrates with carbon dioxide were described in 1994. These studies demonstrated that carbon dioxide has favorable properties for spraying coatings at very high polymer levels. The design of polymers with a relatively high carbon dioxide solubility, allows very-low-solvent and solvent-free coatings to be developed and sprayed. (6)

SPRAY GENERATION AND CONDITIONS

The supercritical fluid spray process uses specifically designed spray equipment which meters and pressurizes the coating and carbon dioxide gas respectfully. The supercritical pressures are well within the standard regime of current spray application systems; allowing the use of airless spray guns, hoses,

spray nozzles, and pumps. The supercritical temperatures are well within the coating parameters of conventional heated paint systems. Because there is no need for exotic spray equipment, a wide selection of previously developed accessories for other paint systems and lines can be utilized.

In order for carbon dioxide (which is a gas under normal conditions) to be dissolved in the coating formulation, it is necessary to pressurize the mixture to maintain the supercritical conditions (1200 - 1600 psig). These conditions are well within the standard regime of current spray application systems. For carbon dioxide to be supercritical and offset the cooling which occurs as carbon dioxide diffuses from the solution as a free gas in the spray, the solution is heated. The typical range is from 40 to 70 degrees Celsius (100 to 160 degrees Fahrenheit). The carbon dioxide is used at a level which gives a decompressive spray with the desired atomization and film properties. The dissolved carbon dioxide usually reduces the spray viscosity to less that 50 centipoise. The coating material usually has a formulated viscosity from 800 to 3000 centipoise, but materials as high as 100,000 centipoise have been successfully sprayed. As for the adhesion promoter, the material was sprayed at 20,000 centipoise

The amount of viscosity reduction is a function of the polymer system, temperature, pressure, carbon dioxide concentration, and solubility. The viscosity reduction is important because it allows the spray solution to be readily atomized into fine droplets necessary to deposit a high quality, uniform coating film. The supercritical carbon dioxide is used at a level that gives a decompressive spray with the desired atomization and film deposition characteristics. This can vary from 10 to 50% by weight of the spray mixture, depending on the solubility, solvent level, pigment level, spray temperature, and spray pressure.

Another unique feature of the supercritical fluid spray process is the carbon dioxide level in the spray mixture can be used to regulate the film build and to some extent, its dry time. When spraying at constant pressure through any given nozzle of fixed flow, increasing the concentration of carbon dioxide reduces the deposited film thickness. As the film thickness decreases, so does its dry time. When a constant film thickness is required, the dry time can be reduced by increasing the concentration of carbon dioxide in the spray mixture. This has the same effect as increasing the overall relative evaporation rate (RER) of the total solvent blend. This effect of increased carbon dioxide on reduced dry time is most noticeable in lacquer coating systems. Conversely, the dry time can be extended by simply reducing the carbon dioxide concentration in the spray mixture. Thus allowing a single coating formulation to be successfully spray applied across a broad range of ambient conditions without the need for solvent additions or extending the production line for longer dry times.

SPRAY CHARACTERISTICS

Supercritical carbon dioxide functions both as a viscosity reducer and a generator of vigorous atomization. This vigorous atomization is produced by a new decompressive mechanism that remedies the defects of airless spraying. This new decompressive spray produces a high quality, uniform film. Conventional airless spray techniques are often characterized by coarse atomization and defective spray fans that limit their usefulness to the application of low - quality films. The conventional atomization mechanism employs a high pressure drop across the spray orifice to generate a high-velocity liquid film.

The film becomes unstable when the shear between the high velocity film and the surrounding air exceeds the surface tension and cohesive forces in the film. When the shear is high enough, the film disintegrates into a series of droplets. Because the surface tension and cohesive forces in the film are not completely overcome, the spray consists of nonuniform size droplets. The spray fan tends to contain jets which limit the ability to deposit a high quality, uniform film.

Even though the spray produced using carbon dioxide is airless in nature, it has all of the desirable traits of air spray, without high air volumes. A feathered spray, with the spatial uniformity of fine droplet sizes necessary for obtaining high quality films and high transfer efficiencies, is produced from the vigorous decompressive atomization provided by carbon dioxide. Due to the finer atomization produced by the supercritical spray than conventional airless sprays, a carefully controlled experiment was conducted comparing the airless supercritical spray fluid to air spray. (7)

The vigorous decompressive atomization is believed to be produced when the dissolved supercritical carbon dioxide in the spray solution suddenly becomes exceedingly supersaturated as the spray exits the nozzle and undergoes a rapid and large pressure drop. The dissolved carbon dioxide is driven forcefully to the gaseous state. The rapid gasification of the carbon dioxide overwhelms the surface tension and cohesive forces of the spray solution before a liquid film can form at the nozzle. By disrupting the formation of the liquid film, the defects of the airless film are avoided. Because the fan is no longer constrained by the surface tension and cohesive forces of the airless fan, a wider fan is generated at the nozzle exit. This permits the formation of a rounded parabolic - shaped spray fan with high uniformity of droplet sizes.

The fan is characterized by tapered edges similar to those of conventional air spray fans. The tapered edges permit the coating material to be deposited uniformly in a wide central region, with progressively less coating deposited towards the edges of the fan. This is particularly desirable when there is a need to overlap

adjacent layers of sprayed coating to produce a uniform film thickness. More importantly, by further optimizing the adhesion promoter, it could also be applied electrostatically to fully utilize the parabolic spray and wrap the part for a more tailored application. The fan widths of the spray are regulated by nozzle selection, as is done with conventional airless spray.

Decompressive atomization can produce fine sprays that are in the same size range as air spray systems and rotary atomizers. Laser light scattering measurements show that average droplet sizes are typically in the 20 to 50 micron range, although much smaller and larger sizes can be produced if desired. Furthermore, the droplet size distributions can be quite narrow, which is highly desirable to obtain both high quality coatings and high transfer efficiency .

The most significant difference between SCF and air spray is the widths of the droplet size distributions, as compared in Figures 1-3. The droplet size of 35 microns (sauter mean diameter) and a narrow distribution in Figure 1 having by volume only 1% large droplets and 11% small droplets is characteristic of the SCF spray. For comparison, the air spray was adjusted to the same average size in Figure 2. This, however, produced a very broad distribution having relatively large fractions of large droplets (22%) and small droplets (19%).

Whereas the decompressive spray would produce an excellent appearance, the corresponding air spray would produce an unacceptably poor appearance because of the many large droplets. In order to reduce the fraction of large droplets to an acceptable level (3%), atomizing air flow was increased. Even though this did reduce the larger particles, it also produced much smaller spray particles. These smaller particles of about 20 microns (35%) would significantly lower the transfer efficiency as in Figure 3. In order for air spray to achieve equal appearance to SCF spray, air spray could have a substantially smaller average droplet size than decompressive sprays.

Conversely, by overatomizing the coating to reduce the larger droplets, this creates smaller droplets that became overspray and reduces transfer efficiency. In contrast to the decompressive spray, the narrow droplet size distribution produces both good appearance and high transfer efficiency. Coating quality deteriorates significantly as the number and size of the largest droplets in the spray increase above a low level. The acceptable level depends on coating thickness. Generally, it is desirable to minimize the population of droplets above about 70 microns in size. Transfer efficiency decreases rapidly when the droplet size is below about 10 microns. When droplets become too small for inertial and electrostatic forces to transport droplets to the substrate, they are lost as overspray. The decompressive sprays often have 90 to 96% of the droplets between 12 and 65 microns in size.

Droplet Size Distribution Comparison Between SCF Spray and Air Spray

Figure 1

A. CO_2 DECOMPRESSIVE SPRAY

35 MICRON AVERAGE SIZE

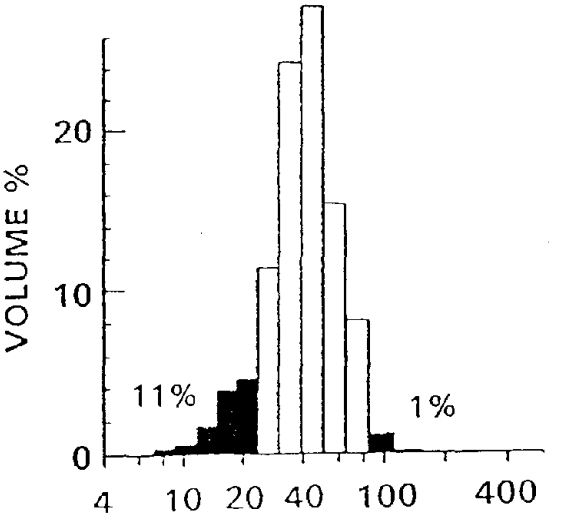


Figure 2

B. AIR SPRAY HAVING SAME AVERAGE DROPLET SIZE

35 MICRON AVERAGE SIZE

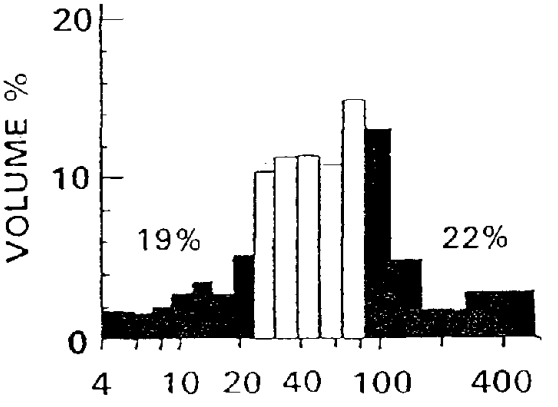
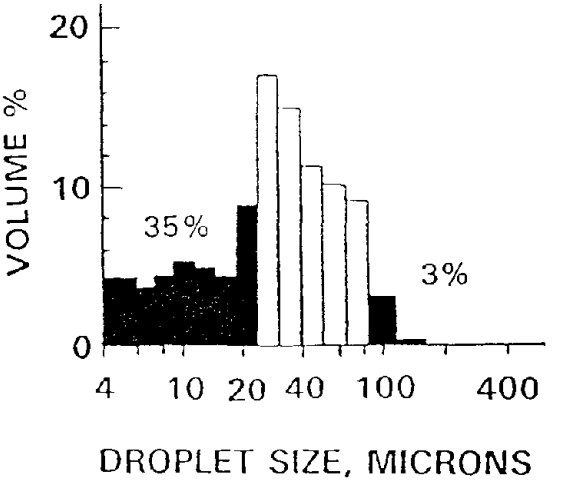


Figure 3

C. AIR SPRAY HAVING HIGH ATOMIZING AIR FLOW TO ELIMINATE LARGE DROPLETS

LOW AVERAGE DROPLET SIZE



Furthermore, the decompressive atomization produces a spray that is highly spatially uniform in droplet size, whereby the droplet size varies very little with position in the spray. The measured droplet sizes are constant along the major and minor axes of the spray and they do not change with distance from the spray tip. Spatial uniformity in droplet size is highly desirable for obtaining high quality coatings and higher transfer efficiency, because it gives a narrower overall droplet size distribution for the entire spray. Thus eliminating portions of the spray that have too coarse or too fine atomization.

SCF ADHESION PROMOTER OPTIMIZATION

The coating used in the supercritical fluid (SCF) process was designed from a commercially used adhesion promoter. The SCF adhesion promoter is at higher solids and contains a different solvent composition than the conventional formulation. The volume solids for the conventional formulation are 7.5%, whereas the volume solids for the SCF formulation are substantially higher at 20.6%. Because of the dramatic reduction in the solvent content of the SCF adhesion promoter, solvent reformulation was necessary to obtain a high quality coating with good flow and leveling properties. A comparison of the physical properties of the solvent blends for the conventional and SCF formulated coatings is shown in Table 1.

Table 1

Solvent Blend Properties	Conventional Adhesion Promoter	SCF Adhesion Promoter
Density	7.23 lb/gal	7.27 lb/gal
Relative Evaporation Rate (RER)	56.4	26.6
Non-Polar Solubility Parameter	8.02	7.94
Polar Solubility Parameter	3.74	3.40
Hydrogen Bonding Solubility Parameter	0.41	0.66

The solvents used for the SCF formulation have similar solubility parameters to those used in the conventional formulation. The major difference between the two formulations is the relative evaporation rates (RER). The conventional solvent blend has a much faster evaporation rate (RER=56.4) than the SCF solvent blend (RER=26.6).

APPLICATION RESULTS

The SCF application of adhesion promoter on TPO bumpers was initially trialed at the Ford Milan plant in Michigan in 1994. The objectives were to determine product performance; VOC reduction; and application effectiveness. The SCF adhesion promoter was applied to TPO bumpers at a dry film thickness of 0.3 mils. The applied film is smoother and also exhibits less orange peel than the conventional film applied with HVLP spray guns. The material utilization of the SCF applied adhesion promoter was found to be much better than the conventionally applied HVLP adhesion promoter. The transfer efficiency improved from approximately 28% for the conventional process to about 38% for the SCF process. This dramatic improvement allows applicators to spray substantially higher solids paint using the SCF process and greater latitude for achieving the desired film build.

The transfer efficiency improvement coupled with the higher solids formulation for the SCF process also results in significant VOC reduction. The pounds of solvent emitted per gallon of solids applied (GSA) is calculated at approximately 323 for the conventional process and 77 for the SCF process. This represents a 76% reduction in emissions. By combining the SCF process with oven incineration, an even greater reduction in the VOC of the coating formulation can be achieved. The solvent emissions in the spray booth and oven can be estimated for each coating formulation by using a proprietary state-of-the-art computer program.

The computer program takes into account room temperature evaporation of solvent (spray booth), elevated temperature evaporation of solvent (oven), polymer-solvent interactions, solvent-solvent interactions, diffusion of solvent through a film, and film thickness. Based on this modeling, approximately 98% of the solvent in the conventional formulation is emitted in the spray booth, while for the SCF formulation, only 64% of the solvent is emitted in the spray booth. Specifically, the SCF process shifts the solvent emission from the spray booth to the oven. If the solvent emitted in the oven is incinerated, the SCF process leads to an even higher reduction in solvent emissions. The solvent emissions for the conventional and SCF formulations are summarized in Table 2.

Table 2

	Conventional Adhesion Promoter	SCF Adhesion Promoter
% Volume Solids	7.5	20.6
% Transfer Efficiency	28	38
VOC (LBS/Gallon)	6.8	6.1
VOC (LBS/Gallon of Solids Applied)	323.8	77.9
Solvent Split		
% Booth	98	64
% Oven	2	36
Booth Overspray (LBS/GSA)	233.1	48.3
Booth Solvent Split (LBS/GSA)	84.8	18.9
Oven Solvent Split (LBS/GSA)	1.9	10.7
Total Emissions, LBS/GSA (Without Oven Incineration)	323.8	77.9
Total Emissions, LBS/GSA (With Oven Incineration)	321.9	67.2

PERFORMANCE TEST RESULTS

Several tests were performed on both compounded and reactor grade TPO plaques prepared as illustrated in Figure 4. The polyurethane basecoats and clearcoats were applied using standard conventional air atomized spray. Painted plaques were tested after a 72 hour ambient air postcure. All testing passed as illustrated in Figure 5.

FIGURE 4
STEPS UTILIZED FOR TPO PLAQUE PREPARATION
AND COATINGS APPLICATION

1) No pretreatment or powerwash, air blow off only
2) Application of adhesion promoter
3) 2 to 3 minute ambient air flash
4) 30 minute bake @ 250°F
5) 10 minute cooldown
6) Application of polyurethane basecoat
7) 5 minute ambient air flash
8) Application of polyurethane clearcoat
9) 10 minute ambient air flash
10) 30 minute bake @ 180°F

FIGURE 5
TEST RESULTS USING THE SUPERCRITICAL FLUID SPRAY PROCESS
FOR ADHESION PROMOTER

TEST	COMPOUNDED TPO	REACTOR TPO
Adhesion	PASS	PASS
Water Immersion (240 Hrs.)	PASS	PASS
Gas Drip Resistance	PASS	PASS
Flexibility @ 23°C (21, Mandrel)	PASS	PASS
Flexibility @ -20°C (31, Mandrel)	PASS	PASS
Thermal Shock	PASS	PASS
H_20 Spot	PASS	PASS
Soap Spot	PASS	PASS
UBC Spot	PASS	PASS
Acid Spotting	PASS	PASS
Chemical Resistance		
Motor Oil	PASS	PASS
Tar & Road Oil Remover	PASS	PASS
WWF	PASS	PASS
Chip Resistance	PASS	PASS
Heat Resistance	PASS	PASS
Resistance to Scuffing (5000 cycles)	PASS	PASS

CONCLUSION

Thus far, test results show that the supercritical fluid spray (SCF) process can be used to reduce the VOC of a solvent borne adhesion promoter without affecting adhesion performance on TPO bumpers and plaques in both laboratory and production settings. The supercritical fluid process meets performance criteria; surpasses regulatory standards for automotive plastic component adhesion promoters; and is proving to be a very effective approach for achieving these goals.

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SESSION 7B

WOOD FURNITURE TECHNOLOGIES

PAPERS PRESENTED:

"Demonstration of No-VOC Wood Topcoat"
by
Eddy Huang
AeroVironment
Monrovia, California

"Evaluation of Supercritical Carbon Dioxide Spray Technology to Reduce Solvents in a Wood Finishing Process"
by
Paul Randall
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Cincinnati, Ohio

"Evaluation of Alternative Chemical Strippers on Wood Furniture Coatings"
by
Sonji Turner
Research Triangle Institute
Research Triangle Park, North Carolina

DEMONSTRATION OF NO-VOC WOOD TOPCOAT

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INTRODUCTION

The worldwide coatings market is estimated to be in excess of $34 billion annually. The U.S. market is about $14 billion segmented in three main categories: (1) Architectural Coatings (AC); (2) Product Coatings used by original equipment manufacturers (PC-OEM); and (3) Special Purpose Coatings (SPC). In most markets, customers' needs are being satisfied by a relatively small number of coatings companies, many with sales approaching $1 billion. A significant number of coatings operations are part of large chemical groups such as AKZO, Ashahi, BASF, DuPont, ICI, Mitsubishi, and PPG Industries. The industry also includes a number of very large independents, like Beckers, Jotun, Kansai, Lilly, Nippon Oil & Fats, Nippon Paint, Reliance, Sadolin, Sherwin Williams, and Valspar. The profile of the coatings industry and the markets it serves has undergone dramatic change in the last decade. The strongest thrusts have been forced by such things as huge business realignments, consolidations and reductions in the number of coatings companies, and the impact of environmental compliance.

The U.S. Environmental Protection Agency (EPA) has implemented regulations to minimize or eliminate the emissions of volatile organic compounds (VOCs). It is estimated that the annual U.S. market for wood coatings is approximately 240,000 m^3 (63 million gallons).[1] On this basis, between 57 and 91 million kilograms (125 and 200 million pounds) of VOCs are emitted into the air each year from the use of presently used waterborne and solvent-borne systems.

The objective of this project was to develop a new low-/no-VOC wood topcoat through continuing research, formulation adjustments, and application testing. Efforts were dedicated to conduct joint research into new promising technologies that are sufficiently mature for demonstration to wood product manufacturers. The high value-added coating products were developed utilizing existing technical know-how, data, and patents related to the new technology.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

DISCUSSION

Background

EPA and state environmental agency actions to lower VOC emissions have had an effect on the marketing of coatings, and the organic and inorganic binders which are widely used in the industry. Some companies seek to qualify coatings thinned with "conforming" solvents (solvents not photochemically reactive) such as chlorinated hydrocarbons. One of these solvents, 1,1,1 trichloroethane, is no longer a feasible compliance option since it has been found to be a hazardous air pollutant (HAP) and to contribute to global warming. Other companies have pursued latex-based, water-dispersed coatings even though they do not currently meet chemical resistance, during those critical first days after application, and drying rate specifications . Many waterborne coatings rely on coalescing agents to achieve a smooth cured film (eliminate "orange peel"). (Ethylene glycol ethers, often used as coalescing agents, are HAPs.) As research continues, there are an increasing number of durable waterborne and water- reducible coatings which are free of coalescing agents. Finally, there is a resurgence of interest in solvent-free coatings (e.g., powder and radiation cured coatings), which would probably not have reached such research intensity were it not for the air, water, and toxicity legislation on state and federal levels.

The wood coating industry can be separated into two categories having different requirements with respect to application technique.[2] These are flat stock coating, and the coating of three dimensional objects. Flat stock is usually coated on a continuous coating line of some type, and more complicated three dimensional objects, such as furniture, usually require spray application and batch drying. The kitchen cabinet industry uses nitrocellulose (N/C) for the high end or conversion varnish/conversion lacquer (also called acid catalyzed) coatings for the bulk of its finishing needs. Conversion varnishes and lacquers contain up to 50% of urea or melamine formaldehyde resins which are only partially cured at the low temperatures allowable for wood surfaces. In addition, formaldehyde may be formed as a reaction product during curing. Thus formaldehyde emanates from the coating throughout its use life as well as during the coating process. Formaldehyde has been designated by the EPA and California Air Resources Board as a probable carcinogen. The N/C must be replaced to meet VOC regulations and the uncured urea/melamine formaldehyde containing coatings replaced due to the formaldehyde emissions.

Water-based products have been introduced to much of the lumber industry to replace the high VOC materials previously used on plywood, hardboard, particle board, and regenerated wood-finger jointed wood products. These products, however, are a full step down in performance properties such as hardness, toughness, adhesion, and solvent and stain resistance. Their second weakness is in energy consumption; i.e., they require long time/temperature exposure for cure. They may or may not result in formaldehyde emissions.

The South Coast Air Quality Management District (SCAQMD) "Rule 1136 - Wood Products Coatings" regulates the allowable VOC concentration of wood coating products. It is estimated that compliance throughout the SCAQMD jurisdiction with these rules would reduce VOC emissions by about 18 Mg (20 tons) per day. By phasing in low-VOC coatings, instead of requiring installation of add-on controls, SCAQMD believes that furniture manufacturers will be

able to comply with SCAQMD's rules without increased costs. Rule 1136 currently limits the VOC content to 680 g/ℓ of clear topcoat and 600 g/ℓ of pigmented coating, less water and less exempt compounds. (Unless otherwise stated, all VOC content data in this paper are less water and exempt compounds.) A final compliance limit of 275 g/ℓ for both clear topcoats and pigmented coatings is currently set to take effect by July 1, 1995.[3]

A new zero-VOC wood topcoat which consists of an epoxy component and an amine curing component was patented by Adhesive Coatings Co. (ADCO), San Mateo, California. The complete absence of organic solvents means that this new topcoat not only less hazardous to use but emits practically no VOCs and therefore does not significantly contribute to air pollution.

A new two-component water-based epoxy wood coating system, based on the new, ADCO topcoat chemistry developed in this project, has the potential to replace a very significant share of current organic solvent systems in use. As will be discussed later, the new zero-VOC topcoat's high gloss and excellent chemical resistance properties are ideal for the wood manufacturing industry for flat stock, for particle, chip, and wood flower products; spray primers for door skins; and finishing systems for interior wood products such as furniture and kitchen cabinets. This material can be manufactured using readily available raw materials and standard resin manufacturing equipment without polluting the atmosphere.

To date, substantial progress has been made in identifying market opportunities for new environmentally sound products. In addition to the research and development of a new zero-VOC wood topcoat, a marketing plan of the developed product was included as part of this development project. This included working with the manufacturers and suppliers to develop a marketing plan to get the products into use by the public.

Coating Characteristics

The most important properties for low-VOC coating technologies are:

* "Dial-a-Cure" (control cure speed through selection/matching of curing agent)
  - ultra-fast cure (air cure in minutes)
  - high speed application (forced cure in seconds)

* Friendly to adverse application conditions
  - cures under broad temperature range
  - cures on wet or dry surfaces

* Liquid
  - water emulsions with water as the continuous phase, no solvents, no keying agents, no film coalescing aids present or required
  - high solids

* Environmentally sound
  - water reducible & water cleanup of materials
  - no solvent (low-VOC)

- no or very low formaldehyde emissions
- no free isocyanate

The new two component water-based epoxy topcoat developed in this project has the potential to meet the performance of the solvent-based system and can replace current solvent systems. The attractive coatings properties which make them promising can also be applied in the wood products area. These properties include:

* low or no formaldehyde
* extreme water and chemical resistance
* very fast cure
* liquid at high solids
* low temperature cure
* no solvents and thus low-/no-VOC.

The new ADCO wood topcoat is a two-part, chemically cured, water reducible, air dry epoxy coating for use as a durable coating for wood surfaces and wood products. It can be used as a sealant and as a high gloss, durable topcoat that gives a lacquer like, clear finish. The complete absence of organic solvents in the formulation or their formation during curing, results in zero emission of VOCs and HAPs. The self-contained manufacturing process also emits no significant air pollutants. The polymer/curing agent screening matrix, performance characteristics, and chemical/stain resistance of this no-VOC topcoat are discussed in the following section.

Polymer Formulation Testing

Polymer variations of ADCO's basic EnviroPolymer (A) in combination with each of several proprietary curing agents (B) were conducted. All combinations contained low or no VOCs. Up to eight different ratios were evaluated for each combination, and the best ratio observed was then selected for further evaluation by applying this coating on solid oak.

Four variations of EnviroPolymer A-1 (EP 180-60), A-2 (EP 200-60), A-3 (EP 510-60), and A-4 (EP H-60) were used in this project. Four proprietary curing agents B-1 (80-70), B-2 (65-71), B-3 (65-99), and B-4 (81-93) were identified as being the most likely to yield promising results. The initial ratings used to identify the most promising ratios for further evaluation were (1) excellent/very promising, (2) good/somewhat promising, (3) fair/possible, and (4) poor/unlikely (see Table 1).

Formulations A-1/B-2 and A-2/B-1 were judged to be the most likely to yield promising test results when applied to a substrate for further determination of the coatings performance characteristics (dry time, gloss, parallel groove adhesion, scrape/mar, and chemical and stain resistance). Dry time was measured as the amount of time that was taken for the coating to harden before it could be sanded and re-coated. To be objective, a gloss meter was used to put a measured value on the degree of gloss. The method described in ASTM D 523[4] was followed.

TABLE 1. POLYMER/CURING AGENT SCREENING MATRIX				
	A-1	A-2	A-3	A-4
B-1	Good	Excellent	Poor	Poor
B-2	Excellent	Good	Fair	Poor
B-3	Good	Good	Good	Good
B-4	Good	Good	Good	Fair

Evaluation of adhesion to different surface treatments, or different coatings to the same treatment is extremely important to the furniture manufacturing industry. The method described by ASTM D 3359[5] was followed. After parallel grooves were cut into the coating, tape was applied over the grooves and removed. The cross-hatch pattern was inspected through a magnifying glass and rated against the standards. Gt 0/5B was the best rating followed by Gt 1/4B, Gt 2/3B, Gt 3/2B, Gt 4/1B, and Gt 5/0B.

A modified ASTM D 2197 method[6] was followed to differentiate the degree of coating hardness. After complete curing, the scrape/mar resistance was determined by pushing the panels beneath a round stylus or loop that was loaded in increasing amounts until marring of the coatings was detected.

Resistance to various household chemicals is an important characteristic of wood furniture finishes. The methods described by ASTM D 1308[7] were followed. This evaluation covers the effects household chemicals have on organic finishes such as discoloration, change in gloss, blistering, softening, swelling, and loss of adhesion.

A cooperative study on the evaluation of low-VOC coatings for wood furniture showed that several water-based clear topcoats meet the VOC content requirement 275 g/ℓ.[8] The performance characteristics of this new zero-VOC coating were compared with those of other low-VOC waterborne coatings in Tables 2 and 3. From Table 2, this new zero-VOC coatings showed excellent performance characteristics in terms of adhesion, dry time, gloss, and scrape/mar resistance. The scrape/mar resistance was especially remarkable (twice as good as the average of other waterborne coatings).

SCAQMD method 304-91 (Determination of Volatile Organic Compounds (VOC) in Various Materials) was used to conduct VOC analysis.[9] ASTM D 1475[10] was used to determine the density of coatings. Total volatile content was measured by ASTM D 2369[11] and water content was determined by ASTM D 3792.[12]

Market Analysis

The wood coating market is segmented by the industry into wood-furniture, fixtures, and wood-factory finishing. These segments in turn are sub-segmented into wood furniture, kitchen

TABLE 2. PERFORMANCE CHARACTERISTICS OF LOW-/NO-VOC COATINGS				
Manufacturer/ Topcoat	Adhesion	Dry Time (minutes)	Gloss 60^{o} Sheen	Scrape/Mar (grams)
ADCO Topcoat	GT 0/5B	20-25	80.0	1050
AKZO 680-60C018-115 W/B	GT 0/5B	30-35	34.3	300
AMT 01TC-0090-50 W/B	GT 0/5B	30-35	62.0	500
GUARDSMAN 45-1065-40 W/B	GT 0/5B	30-35	46.8	800
LILLY 787W43 W/B	GT 0/5B	30-35	23.9	300
PINNACLE 137-CL-1	GT 0/5B	30-35	79.4	500
SHERWIN-WILLIAMS T70C510 W/R	GT 0/5B	30-35	44.0	500
SINCLAIR WL 14-9	GT 0/5B	30-35	38.6	400
WATERCOLOR Topcoat	GT 0/5B	30-35	37.1	600

TABLE 3. CHEMICAL AND STAIN RESISTANCE OF LOW-/NO-VOC COATINGS					
Manufacturer/ Topcoat	Acetone[a]	Coffee	Mustard	Hot Tap Water	Nail Polish Remover
ADCO Topcoat	1	1	2	1	2
AKZO 680-60C018-115 W/B	3	1	2	1	2
AMT 01TC-0090-50 W/B	2	1	2	1	2
GUARDSMAN 45-1065-40 W/B	2	1	2	1	3
LILLY 787W43 W/B	2	1	2	2	3
PINNACLE 137-CL-1	2	1	2	1	1
SHERWIN-WILLIAMS T70C510 W/R	2	1	2	1	2
SINCLAIR WL 14-9	2	1	2	1	2
WATERCOLOR Topcoat	1	1	1	1	2

a. 1 = no effect, 2 = slight effect, 3 = medium effect

cabinet, new case goods, plywood/hardboard/regenerated wood products, flat stock finishes, and specialty product finishes. The furniture industry is faced with a dilemma. Other than special small segments of the paper coating industry, wood furniture coatings consume almost 100% of the nitrocellulose coatings produced. The coatings, by the very nature of the high intrinsic viscosity of nitrocellulose, are very low in solids and thus are very high in solvent and high VOCs.

The high emission rate has caused the loss of all operating permits in some states and some permits in every state; and wood furniture manufacturers are either moving off-shore or concentrating in the Southeastern U.S. Radiation-cure techniques and coatings have made some penetration, although small, because the shape of the item produced does not lend itself as readily to use of existing technology such as ultraviolet (UV) or electron beam (EB) equipment. One approach used by the furniture industry to "stay-in business" has been introduced in Europe. This is a modified case goods approach where most of the pieces are prefinished in flat stock. The piece of furniture is then assembled and given a final finish and touch-up. The coating used for the flat stock pieces is a low-VOC content radiation-cured product. The final finish, however, is likely to be high VOC content N/C. The new zero-VOC topcoat developed in this project meets the same cure rate without the radiation equipment investment cost, hazard to the eyes of the employees, and skin sensitivities. In addition the complete finish can be applied after assembly, if desired.

In the zero-VOC wood coating market research, the needs for new products were discussed with the leaders in the manufacture of regenerated wood products; i.e., particle board, chip board, and wood flake products. There are many product opportunities for application of this new technology. Efforts were focused on such promising possibilities as binders for particle, chip, and wood flower products; spray primers for door skins; surfacers for concrete form boards to replace paper laminate; and finishing systems for interior wood products such as furniture and kitchen cabinets.

It is anticipated that the zero-VOC wood topcoat developed in this project will set new industry standards by addressing the following manufacturers' problems:

* The formaldehyde problem. All manufacturers seek low or no formaldehyde exposure to their employees; the atmosphere surrounding the manufacturing site; and the customer or user.

* Lower moisture transmission problem. All manufacturers seek to reduce the degradation caused by swelling and warping from changes in product dimension from water penetration.

* Exterior market problem. All manufacturers seek to upgrade their product line to achieve penetration in the exterior product market.

* The down-time cleanup problem. All manufacturers of regenerated board must shut down periodically for cleanup to reduce the unacceptable green board

rejection rate and fire hazard.

* The energy problem. All of the products used by the mills require extensive time/temperature cure or drying cycles. Low temperature or fast air dry would lend improved economics to the industry and/or provide a large competitive advantage over the competitors.

* The toxic air emissions problem. Some facilities in the furniture industry may use water-based formulations which contain toxic compounds, most notably, ethylene glycol ethers.[13] Most waterborne wood coatings used glycol ethers in their formulations to stay in compliance.

Most wood furniture is finished with nitrocellulose resin-based coatings averaging 750 g/ℓ VOC and 375 g/ℓ hazardous air pollutants (HAPs). In the finishing of an average dining room table (4 ft X 6 ft), about 9 kilograms of VOCs and 4.5 kilograms of HAPs are emitted. While progress has been made to formulate low-VOC coating systems, many of these use ethylene glycol ethers, which are more toxic than most of the solvents used with nitrocellulose systems. Based on the South Coast Air Quality Management District/Southern California Edison/California Furniture Manufacturers Association Cooperative study of low-VOC coatings for wood furniture, the VOC/air toxic compounds contained in the commercially available water-based clear topcoat were evaluated. In Table 4, the VOC/air toxic contents of ADCO's new zero-VOC coating were compared with commercial coatings which met the VOC content requirement of 275 g/ℓ.

Many resin and coatings manufacturers have done research on very low-VOC coatings for the wood furniture industry. Penetration into the market place has been slow. Without regulatory pressure, there is no incentive to switch from traditional high-VOC nitrocellulose coating systems.

Several wood furniture manufacturers and coating suppliers were contacted to identify wood coating concerns, current application methods, costs, and critical areas for product improvements. Marketing information related to the wood coatings market was collected. This information was reviewed to establish what specific data still need to be collected and how they should be used in structuring the planned market survey of wood coating suppliers. The product marketing discussions have centered on how to commercialize specific low-/no-VOC finished coating applications resulting from this wood coating project.

CONCLUSIONS AND RECOMMENDATIONS

The resulting topcoat showed excellent performance characteristics in terms of adhesion, gloss value, dry time, hardness, level of solvents, and chemical/stain resistance in laboratory development tests. The VOC contents of both the clear topcoat and the white pigmented topcoat were less than 10 g/ℓ, the detection limit of the test method. This coating's performance and properties in finished material were compared favorably with other low-VOC waterborne wood coatings.

TABLE 4. VOC/TOXIC COMPOUNDS CONTAINED IN WATERBORNE COATINGS			
Manufacturer/ Topcoat	VOC (g/ℓ)	HAPs	
		Name	Weight (%)
ADCO Topcoat	<10[a]	None	0
AKZO 680-60C018-115 W/B	210	Ethylene Glycol Monobutyl Ether Diethylene Glycol Monobutyl Ether	6.2 3.9
AMT 01TC-0090-50 W/B	240	Propylene Glycol N-Butyl Ether	1-10
GUARDSMAN 45-1065-40 W/B	270	Diethylene Glycol Monobutyl Ether Propylene Glycol N-Butyl Ether	6.0 3.0
LILLY 787W43 W/B	240	Propylene Glycol N-Butyl Ether	3.4
PINNACLE 137-CL-1	270	Triethylamine Ethylene Glycol Monobutyl Ether Diethylene Glycol Monobutyl Ether	<5.0 3.0 3.0
SHERWIN-WILLIAMS T70C510 W/R	270	Ethylene Glycol Monobutyl Ether Diethylene Glycol Monobutyl Ether	4.8 9.2
SINCLAIR WL 14-9	200	Diethylene Glycol Monobutyl Ether	3.0
WATERCOLOR Topcoat	100	Propylene Glycol N-Butyl Ether	1-10

a. Detection limit of test method.

Demonstration of the new topcoat at one or more furniture manufacturing facilities would be the next step in commercializing this technology. Further development work may be required in parallel with each demonstration to tailor rheology, dry time, etc. to the host's furniture finishing line.

The identification and/or development of compatible low-/no-VOC "stain" and "sealer" wood coatings would provide a complete low-/no-VOC wood coating system.

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EVALUATION OF SUPERCRITICAL CARBON DIOXIDE SPRAY TECHNOLOGY TO REDUCE SOLVENTS IN A WOOD FINISHING PROCESS

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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INTRODUCTION

This project was conducted by the Pollution Prevention Research Branch(PPRB) of the U.S. Environmental Protection Agency(EPA) with the cooperation of Union Carbide Corporation, Nordson Corporation , and the Pennsylvania House Furniture Company. The PPRB is evaluating and demonstrating new technologies for pollution prevention through the Pollution Prevention Clean Technology Demonstration (CTD) Program. (1)

This paper reviews the use of supercritical CO_2 technology for paint spray application. Pennsylvania House Furniture Co. has used supercritical CO_2 coating technology to apply a nitrocellulose lacquer finish to oak and cherry furniture on a chair-finishing line. At current Pennsylvania House production rates, more than 250 furniture units per day are coated with nitrocellulose lacquer by this process.

During the evaluation, three issues of this technology were examined:

- Product Quality: to show that coating applied by this spray technology meets company standards for a quality finish.
- Pollution Prevention Potential: to demonstrate that use of this spray application technology for solvent replacement in coatings reduces volatile organic compounds (VOCs) released during finishing operations.
- Economics: to document the cost to install and operate this technology on an existing spray coating finish line.

Although the research described in this article has been funded wholly or in part by the EPA, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred. Also, mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PROCESS DESCRIPTION

Supercritical fluids are gases that exist at temperatures and pressures near or above the critical point of the fluid as depicted on a phase diagram (Figure 1). At the critical point, the properties of the liquid and the gas are similar or identical. The resulting single-phase fluid exhibits solvent-like properties that can be altered by adjusting temperature and pressure. A number of gases have been examined for use as supercritical fluids in applications such as industrial and analytical separation

processes, cleaning, chromatography, and coating. The UNICARB™ process for coating uses nontoxic, nonflammable carbon dioxide as the supercritical fluid for coating dilution. Carbon dioxide, readily available as a by-product of a variety of industrial processes, has a critical temperature of 31.3°C (88°F) and a critical pressure of 72.9 atm (1070 psi), falling within the ranges already used for heated paint systems and airless spray equipment.

Union Carbide Corporation developed the use of supercritical CO_2 for spray coating applications, introducing this technology commercially in 1988 under the UNICARB™ tradename.(2,3) In the UNICARB™ process, the solvent-like properties of supercritical CO_2 are exploited to replace a portion of the organic solvent in the conventional solvent-borne coating formulation. The supercritical CO_2 acts as a diluent solvent to thin the viscous coating just prior to application, so that the coating can be atomized and applied with a modified spray gun. According to Union Carbide, 30 to 80% of the organic solvent in a coating formulation can be replaced with supercritical fluid. Typically, most of the volatile, fast-drying solvents and some of the medium-drying solvents are eliminated, retaining enough medium- and slow-evaporating solvents to obtain proper leveling and film coalescence. The solvent blends may need to be adjusted to optimize performance with the supercritical CO_2 spray technology. This usually can be done without changing the resin chemistry or pigment-loading levels. The solvent level of even conventional high-solids coatings can be reduced further when applied by this process. The actual reduction in solvent content that can be achieved is dictated by a number of factors. These include the type of coating being applied and its exact formulation, the desired film thickness and properties of the applied coating, and the environment in which the coating is being applied.

Thermosetting, thermoplastic, air-dry, and two-component formulations, in clear, pigmented, and metallic coating systems, have been developed successfully for application by supercritical CO_2 spray technology. Limitations exist with pigmented systems because some of the pigments, (e.g., carbon black), may be soluble in the supercritical CO_2. However, other pigments, including aluminum flake, titanium dioxide, and calcium carbonate, have been included successfully in formulations applied using this process. Nitrocellulose, silicone alkyds, acrylics, and a two-part urethane formulation have been developed for supercritical CO_2 application. Union Carbide is currently working on a two-part epoxy system and a phenolic resin formulation.

The supercritical temperature and pressure of CO_2 are within the ranges already used for heated paint systems and airless spray equipment, but special equipment is needed to introduce the CO_2 into the reduced solvent formulations and then heat and pressurize the resultant mixture prior to spraying. Typically, 10 to 50% carbon dioxide by weight may be introduced depending on the solubility in the coating, the solids level, the pigment loading, and the ambient conditions in the spray booth. Heating lowers the coating viscosity for easier pumping but decreases the solubility of the CO_2 in the coating concentrate. Therefore, optimum operating temperature and pressure must be determined and maintained to achieve the best results in each application.

Usually, the coating is heated to 40° to 70°C with spray pressures of 1200 to 1600 psi. The specially formulated coatings are applied with spray guns similar to those used for airless applications. However, because the decompression of supercritical CO_2 results in finer atomization of the sprayed coating and smaller particles than is common with use of airless spray equipment, slight modification of the spray gun nozzle design was required to optimize the spray pattern. The result is a more finely dispersed and more uniform pattern than typically is achieved with conventional air spray equipment.

Nordson Corporation designed the spray guns used by Pennsylvania House. A supply unit mixes coating concentrate and carbon dioxide to a desired ratio, pressure, and temperature, and delivers the solution to specially designed spray guns. The size of the supply unit is dictated by production requirements. A microprocessor-based controller continuously monitors the system and allows the operator to adjust the ratio of coating concentrate to carbon dioxide for best results. The

supply unit and controller are placed adjacent to, but outside of, the spray booth. The system equipment is available for either manual or automatic operation. Manual and automatic spray guns for electrostatic and non-electrostatic applications can be used with minor modifications to the nozzle. Because the reduced solvent coating is more viscous, a special pumping station is required.

Pennsylvania House uses the UNICARB™ process on the chair-finishing line at its plant in White Deer, Pennsylvania, to apply nitrocellulose lacquer finishes. This supercritical CO_2 spray technology has allowed Pennsylvania House to continue using the solvent-borne nitrocellulose lacquer coating that is used widely in the U.S. wood-finishing industry, while reducing VOC emissions from their finishing operation. To bring this technology to production-line use, Pennsylvania House worked closely with Union Carbide to optimize the basic process, Nordson for equipment-related issues, and with Guardsman and Lilly to optimize the formulations of reduced solvent coatings.

The chair-finishing line at the White Deer facility carries chairs, stools, and mirrors from assembly through the finishing process and to packaging. The finishing process is labor intensive, with manned stations for staining, wiping, rubbing, sanding, polishing, and inspection. The overhead conveyor system runs through the various work stations at 6 to 7 ft per minute; 6 ft per minute is approximately 60-70% of capacity. At this speed, 250-300 units per day are produced. Total time on the line from start to finish is about 4 hours.

Two color stains usually are used to highlight the natural grain and provide color to the wood. Toner stain is sprayed on first, followed by a sprayed mineral-spirit wiping stain, which then is wiped off by hand. Some pieces get a spatter stain for special effects before entering the oven for the first drying step. Oven temperature is maintained at 110°F for all heating steps.The next step is spray application of a 20%-solids nitrocellulose sealer followed by a second pass through the oven. Light hand sanding is performed if needed before or after application of the sealer.

The nitrocellulose lacquer is spray applied next. In the conventional finishing process, nitrocellulose lacquer (21-23%-solids) is applied manually using airless spray equipment in two coats, with a pass through the oven between the coats. Flash-off time between spraying the coating and entering the oven is 10 to 12 minutes. Oven residence time is 7 minutes. The same flash-off and oven-time intervals are used after the second coat of lacquer. Furniture units remain on the line at ambient temperatures for one hour and forty-five minutes after the last oven pass before they are packaged. When the supercritical CO_2 finishing process is used, only one coat of nitrocellulose lacquer is needed to achieve the desired film build and finish quality. The nitrocellulose lacquer formulation optimized for the Pennsylvania House production line has approximately a 41%-solids content. This coating is applied using the UNICARB™ equipment in spray booth #1, followed by a 10- to 12-minute flash-off period, and a 7-minute pass through the oven. Because Pennsylvania House has not reconfigured the chair conveyor line, the UNICARB™ line follows the existing conveyor line through the unused spray booth #2 and the final stage of the oven before reaching inspection and packaging for shipment. The second oven pass is not required for this process but has no negative effect on the cured finish coat.

Conventional and reformulated nitrocellulose lacquer coatings used by Pennsylvania House are supplied to the spray guns directly from the shipping drums. The drums of coating are equilibrated and mixed in the Pennsylvania House paint room before being pumped through lines to the spray booths. Temperature and humidity changes in the plant sometimes require adjustments in the solvent blend of the formulations for optimal spray results. With conventional lacquer, solvent is added to the drum of coating, which then takes about 1 hour to reach the spray booth. This adjustment process sometimes must be repeated to get the desired results. Once extra solvent has been added to a drum of coating, the contents of the drum have a higher volatile content. With the supercritical CO_2 spray system, the

operator simply adjusts the ratio of CO_2 to coating concentrate at the control unit located just outside the spray booth. No additional solvents are introduced into the process, and adjustments are immediately evident.

PRODUCT QUALITY EVALUATION

The specific objective of the product quality evaluation was to determine whether nitrocellulose lacquer applied by the supercritical CO_2 process provides a wood finish of equal or better quality than does the conventional nitrocellulose formulation and spray technique previously used by Pennsylvania House Furniture Company. At Pennsylvania House, the appearance and quality of the final finish are judged through visual examination by inspectors on the coating line. Special attention is given to gloss, smoothness, and the lack of surface defects such as blisters or pinholes.

Product quality was evaluated through subjective evaluations performed by Pennsylvania House staff members and a panel of Battelle coatings personnel. Test substrates were finished on the production lines during an on-site visit. A set of samples was finished using the one-coat UNICARB™ process, and two other sets were finished using one and two coats of the "standard" nitrocellulose formulation and the airless spray equipment still in place on the chair-finishing line. All panels were finished by the same production methods that typically are used on the chair line at Pennsylvania House.

The subjective product quality evaluations demonstrated that a coating applied by the supercritical CO_2 spray process yielded a product with a finish quality equal to or better than the finish quality obtained by conventional materials and methods. Samples finished by the supercritical CO_2 process and by the two-coat conventional process were rated as "acceptable." Samples sprayed with one coat of the nitrocellulose by the conventional process were not acceptable.

In addition to the subjective visual inspections of the test samples, Battelle staff made measurements of gloss(Table 1) using ASTM D529. These measurements provide some quantitative insight into the physical attributes of the finish line of each of the coating processes. The test procedure outlined in ASTM D529 recommends averaging six gloss measurements for a 3-inch x 6-inch sample area, which correlates to 49 measurements on the 7-inch x 21 -inch test substance used here. The mean and standard deviation of the 49 data points represent the overall gloss appearance of each sample, alleviating subjective biases of the person performing the measurements while still incorporating the assessment of any nonuniformity in the gloss across the sample surface. The breadth in standard deviation of the data can be used as a gauge of the uniformity of the sample finish across the complex geometry of the test panels. Gloss test results for each of the nine panels are reported as the mean of 49 determinations and then averaged for each of the sample sets for easy comparison among each of the finishing processes in Table 1. The averaged gloss data for the UNICARB™ samples are statistically the same as those for the conventional two-coat process. The gloss data of both of these sets show that they are substantially glossier than the one-coat conventional finish sample set.

These results are supported by Pennsylvania House records for consumer acceptance. Internal quality control audits on chair-line products show a decrease in finish defects using the supercritical CO_2 system. Based on the number of furniture units requiring rework because of finish defects, product efficiency has improved since the UNICARB™ process was implemented.

POLLUTION PREVENTION POTENTIAL

The pollution prevention potential of this technology is based on reducing the emissions of organic solvents without adding to other wastestreams. The nitrocellulose lacquer finishing process used on the chair line can contribute to pollution in two ways: VOC emissions from the coating formulation, and spray booth wastes, including solvent-laden filters and nitrocellulose "dust". In conventional spray coatings, a blend of fast-evaporating solvents, medium-evaporating solvents, and slow-evaporating solvents are used. In the supercritical CO_2 spray process, most of the fast- and medium-drying solvents are replaced by supercritical CO_2 and the slow-drying solvents are adjusted slightly for better film formation. Although reducing VOC emissions is important, it is equally important to demonstrate the supercritical CO_2 process does not add pollutants to other wastestreams.

Pennsylvania House has been able to reduce the number of coats of nitrocellulose lacquer from two to one. The volume of nitrocellulose lacquer used in each finishing operation was determined during the initial phases of implementing the supercritical CO_2 process at Pennsylvania House. Metering devices were placed in-line on the airless spray guns used to apply the conventional nitrocellulose formulation, and on the coating inlet line to the supercritical fluid supply unit used to feed the coating mixture concentrate and the supercritical CO_2 to the modified spray guns used with the UNICARB™ process.

Pennsylvania House records indicate that it takes approximately 473 ml of the conventional formulation to apply the two coats needed to achieve the desired quality in the finished product. The UNICARB™ process required about 207 ml of the reduced solvent formulation per furniture unit to achieve the same quality. There are two reasons that a smaller volume of coating is required when the supercritical CO_2 process is used: 1. the higher solids content of the UNICARB™ formulation means that more resin is transferred to the substrate per volume of formulation sprayed and 2. the increased viscosity of the film deposited by the process inhibits film buildup by soaking into the wood substrate.

Table 2 compares the volatile solvent content(% by weight) of the two formulations used by Pennsylvania House. The UNICARB™ coating is formulated using 17.5% less solvents (on an absolute basis) than the conventional formulation. Only 9.67% of the UNICARB™ formulation is comprised of Hazardous Air Pollutant (HAP) materials compared to 35.78% for the conventional formulation. On a per-gallon-of-coating-sprayed basis, this difference would result in a relative decrease in VOC emissions of 22.81%, with a 72.97% decrease in HAPs using the UNICARB™ formulation. VOC contents are reported as 563 gms/l for the UNICARB™ formulation and 707 gms/l for the conventional system.

Assuming an average yearly production of 50,000 units and the use of 207 ml for the one-coat UNICARB™ process and 474 ml for the two-coat conventional formulation, the UNICARB™ formulation uses 10,220 liters and the conventional formulation uses 24,604 liters to finish the units. Based on the reported VOC contents, this system change corresponds to an annual reduction in VOC emissions of 67.5% when the newer process is used.

Coating overspray at Pennsylvania House is collected on dry filters that are compressed and stored in 55-gal drums for disposal by landfill. One drum, at a disposal cost of $150/55 gal drum, can hold about 200 compacted filters and solid debris. Waste products generated will include dry and solvent-laden filters and nitrocellulose dust, both loose and trapped in the filters. No liquid waste was generated. Because Pennsylvania House does not separate waste by production lines, no physical data were available for the solid wastestream analysis. However, discussions with Pennsylvania House management and staff consistently indicated that the solid and liquid wastestreams were unaffected by the conversion to the supercritical CO_2 technology.

The chair-finishing process is the same except for the application of the nitrocellulose lacquer finish. Using the old process, two booths were in operation which required cleaning and maintenance. With the UNICARB™ process, only one booth is needed. The transfer efficiency of the modified UNICARB™ spray gun and the air-assisted spray gun are both approximately 50% based on Union Carbide records. However, due to the increased solids content of the UNICARB™ formulation, more solid waste is generated from the overspray by the UNICARB™ process. The 28 dry filters in each of the two spray booths needed for the conventional two-coat finishing process were changed once per week for a total disposal rate of 56 filters/week. The 28 dry filters in the one spray booth required for UNICARB™ finishing are changed twice per week for a total of 56 filters/week. Dry paint and dust from the booths is packed in the disposal drums with the filters, but no increase or decrease in the total volume of these products was noted. Thus, no change was observed by Pennsylvania House in the volume of solid waste generated by converting to the supercritical CO_2 spray process on the chair line.

ECONOMIC ANALYSIS

The objective of the economic analysis was to determine the payback period for the switch to the supercritical CO_2 spray process from the previously used conventional process. The initial investment in capital equipment and installation costs were consider along with the operating costs(materials, waste disposal, labor and utilities). The return-on-investment (ROI) was calculated based on the costs associated with capital expenditures, including equipment and installation, and the return on this investment generated through lower personnel, operating, and materials costs. Details on the ROI calculation are included in the full report.(1)

Implementing the UNICARB™ finishing process on the chair line at Pennsylvania House resulted in substantial annual savings in both utilities and labor as show in Table 3. The annual operating costs were based on the production of 50,000 chairs per year. The UNICARB™ process costs of $ 46,000 include $ 37,000 for the coatings formulation and CO_2 concentrate and $ 9,000 for the CO_2 equipment rental. The conventional formulation costs for the same number of furniture units would be $ 47,000. By converting from a two-coat process to the one-coat process, Pennsylvania House was able to decrease its utility costs by $ 11,000 because there was one less booth to operate. Labor costs were reduced by $ 46,000 because one less finisher and one less sander were needed. Waste handling and disposal costs and finishing line maintenance remained the same for both processes.

Cost savings, realized from a decreased in raw materials costs, were offset by the leasing fees for the CO_2 tank and pump at Pennsylvania House. Additional savings could be realized by decreasing the size of the existing ovens to reflect the change to a one-coat system. Pennyslvania House did not downsize the production ovens to gain gas utility savings.

The annual operating costs of the supercritical CO_2 finish line is approximately $ 58,000 less per year than that of the conventional line. The initial capital investment for the UNICARB™ process was $ 58,000 of which $ 46,000 was for equipment purchase and $ 12,000 for installation of the equipment.

The more detailed economic evaluation found in the full report demonstrates a positive return on investment after the first year with a total payback period with three years if gas utility savings are included, and five years if gas utilities are not included.

CONCLUSIONS

This technology evaluation shows that supercritical CO_2 spray technology has potential as a pollution prevention option in the application of solvent-borne coatings. This technology is not limited to one coating type, but could be used to reduce the solvent level required to spray apply a variety of solvent-borne coatings. The wood furniture facility where this evaluation was conducted maintained product quality with a nitrocellulose lacquer finish and reduced VOC emissions from the coating process. No additional wastes entered the wastestream. Immediate operating savings of $ 58,000/yr were realized. A 100% ROI should be achieved within five years after implementation.

Although the research described in this article has been funded wholly or in part by the EPA, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.
Also, mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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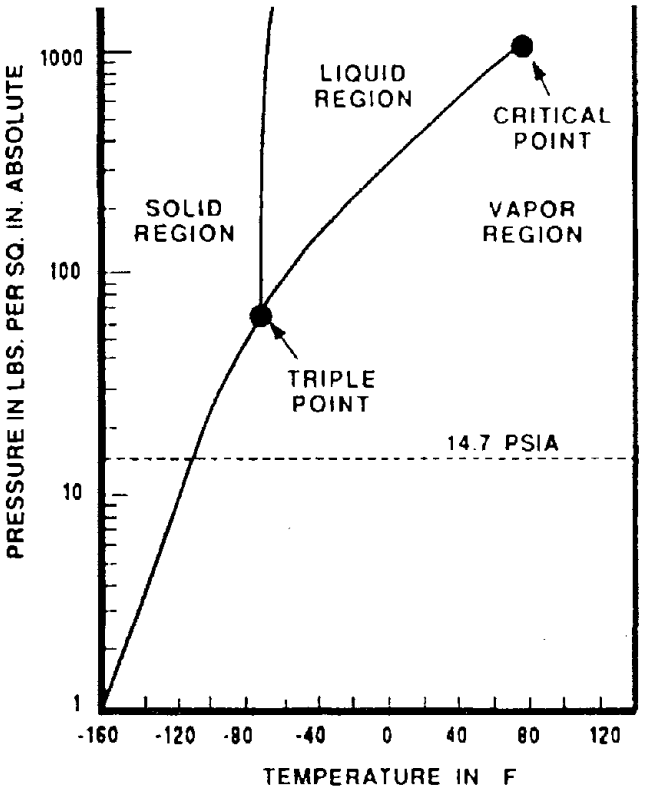

Figure 1. Phase Diagram for carbon dioxide.

* Nielsen, K.A., Busby, D.C., Glancy, C.W., Hoy, K.L., Kuo,A.C., and Lee, C., "Supercritical Fluid Spray Application Technology: A Pollution Prevention Technology for the Future," Union Carbide Chemicals and Plastics Co., Inc. Presented at the 17th Water-Borne & Higher-Solids Coatings Symposium, February 21-23, 1990, New Orleans, LA.

TABLE 1. Gloss data on sample panels

Finishing Process	Sample Number	Average Gloss Data/Panel	Average Gloss Data/Set
Conventional One Coat	46482-9-1	20.3 ± 4.3	20.3
	46482-9-2	20.4 ± 3.1	
	46482-9-3	20.3 ± 3.1	
Conventional Two Coat	46482-10-1	33.2 ± 1.6	32.3
	46482-10-2	35.0 ± 2.2	
	46482-10-3	28.7 ± 2.8	
UNICARB™	46482-11-1	35.3 ± 3.2	31.5
	46482-11-2	30.5 ± 3.1	
	46482-11-3	28.7 ± 2.9	

TABLE 2. Comparison of volatile solvent content of conventional and UNICARB™ coating formulations as percent weight.

Materials Description	HAP (Y/N)	Conventional (% by weight)	UNICARB™ (% by weight)
MEK-heptanone	No		37.25
methoxypropylacetate	No	7.36	
xylene	Yes	16.80	
isopropanol	No	11.20	6.55
toluene	Yes	10.39	
N-butyl acetate	No	11.83	
isobutyl acetate	No	6.89	
2-butoxyethanol	Yes	3.27	9.67
MIBK	Yes	5.32	
isopropyl acetate	No	1.46	
Other		2.37	5.87
Total VOC (% by weight)		**76.88**	**59.34**

Table 3. Summary of Annual Operating Cost Comparing Conventional Finish Line with Supercritical CO_2 Finish Line

Item	Conventional ($/year)	Supercritical CO_2 ($/year)
Coating Materials	47,000	37,000
CO_2 Storage Equipment	---	9,000
Spray Booth #2		
Finish Labor	23,000	---
Sanding Labor	23,000	---
Electricity	11,000	---
TOTAL	104,000	46,000

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Evaluation of Alternative Chemical Strippers on Wood Furniture Coatings

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Abstract: Alternative chemical strippers have been evaluated to determine the potential effects on air emissions resulting from solvent changes in the furniture repair and refinishing industry. Alternative chemical strippers used to remove both traditional and emerging low-VOC (volatile organic compound) wood coatings were evaluated. Phase 1 was a laboratory evaluation of five chemical stripper combinations on three types of coatings. Phase 2 was the assessment of the best performing alternative stripper from the laboratory evaluation in a furniture repair and refinishing facility. This paper discusses both phases of research. Screening and assessment results will be presented at this conference.

Introduction

Chemical strippers employ a variety of chemical mechanisms and may be designed for specific functions. Solvents that cause physical and chemical reactions are often involved in chemical stripping applications. Chemical stripper removal processes encompass cold solvent (acid or alkaline activated), hot alkaline removal, and molten salt baths. These stripping solvents are designed to degrade coating films or destroy adhesion of the film from the substrate to which it is attached (Hahn). In the original equipment and furniture manufacturing markets, chemical strippers are used to remove defective coatings from items that do not pass inspection. They are also used to clean spray booths and coating application equipment. In this study, five alternative cold solvent chemical strippers were used to remove three coating types of wood furniture coatings from wooden surfaces. Following coating removal, the effectiveness of each chemical stripper to remove the coatings from the wooden surfaces was evaluated.

Methylene chloride (CH_2Cl_2) is a halogenated solvent and a suspected carcinogen; however, it is not defined as a volatile organic compound (VOC) by the Environmental Protection Agency's (EPA's) definition. CH_2Cl_2 has been a primary component formulated in chemical strippers. The effectiveness of CH_2Cl_2 is due to its small molecular size, which promotes rapid penetration into the coating film, and to its intermediated solvency for various

polymer coatings. As CH_2Cl_2 penetrates to the substrate, the coating film swells to several times its original volume. The swelling causes an increase in internal pressure at the interface with the coating relieved in a direction away from the substrate. Thus the film wrinkles, blisters, buckles, and bubbles, resulting in its release from the substrate. CH_2Cl_2 has been used in nearly all chemical stripping applications because it can effectively strip a broad range of cured coatings from a substantial variety of substrates (Sizelove, Wollbrinck). Annual estimates for CH_2Cl_2 usage in paint stripping have ranged from approximately 50 million kilograms to 70 million kilograms.

Other solvents and chemicals that are often found in chemical stripper formulations may include: alcohols, xylene, toluene, amines, glycol ethers, mineral spirits, methyl ethyl ketone, acetone, phenol, and benzene (Sizelove, Wollbrinck). These additional components, several of which are VOCs and some of which are hazardous air pollutants (HAPs), are often used to enhance the properties and performance of primary components. In some cases, solvent blends that dissolve the coating film are favored over other types of chemical strippers. Some solvent chemical strippers that employ ketones and aromatic hydrocarbon blends are used primarily where other chemical strippers fail such as on low intrinsic strength films or sharply angled surfaces (Sizelove, Wollbrinck). Annual VOC emission estimates for all U.S. furniture stripping firms have been reported to be as high as 1.1 million kilograms. Alternative chemical strippers have been evaluated to determine the potential effects on air emissions resulting from solvent changes in the furniture repair and refinishing industry.

Project Description

The purpose of this research was to evaluate the feasibility of using alternatives to high VOC/HAP solvent-based chemical strippers that are currently used in the furniture repair and refinishing industry to remove both traditional high VOC lacquer and emerging, low-VOC, wood furniture coatings. Research Triangle Institute (RTI), under a cooperative agreement with the U.S. EPA's Air and Energy Engineering Research Laboratory, screened five alternative chemical strippers, consisting of one industrial and four retail chemical strippers. Alternative chemical strippers were evaluated based on their stripping effectiveness compared to a CH_2Cl_2-based stripper. A panel of individuals experienced in the area of chemical stripping evaluated the samples and selected the most effective chemical stripper for further evaluation. An on-site assessment of the best performing alternative chemical stripper from the screening evaluation took place at a local furniture refinishing facility. The EPA, RTI, several coating suppliers, one chemical stripper supplier, and two local furniture refinishing facilities participated in this project.

Project Objectives

This project was undertaken to identify chemical strippers that could serve as alternatives to CH_2Cl_2-based chemical strippers and to evaluate their effectiveness for the removal of furniture coatings typically used on wooden substrates encountered in furniture refinishing industries. The specific objectives of this research were to:

1. Conduct a laboratory evaluation of the performance of five alternative chemical stripper formulations and compare their performance to the performance of a traditional solvent-based chemical stripper formulation on three coating types found on wood furniture substrates.

2. Assess, in a furniture refinishing facility, the use of the best performing alternative stripper on traditional furniture coatings and new emerging low-VOC furniture coatings.

This project was limited to conducting a screening study and assessing of one industrial and four retail chemical strippers following the recommendations of the manufacturer or supplier of the material. No provisions were made for extending the experiments to cover the modifications of the five chemical strippers, or for the formulations of the chemical strippers. Refinement in the formulation of effective chemical strippers, and a thorough evaluation of the health and environmental effects, were beyond the scope of work for this project.

Project Activities

The laboratory evaluation, the first objective, involved cold, solvent strippers; no thermal methods were used. Solvent strippers work solely by dissolving the coating film. Their dissolving mechanism causes them to become rapidly saturated with dissolved coating. Care must be taken to prevent redeposition of the film on the substrate. Cold strippers act best when they are not true solvents of the film, but are absorbed by the film. This action is similar to the actions of CH_2Cl_2-based strippers. Five chemical strippers and three coating types were selected cooperatively by the EPA and RTI. The selected strippers consist of a combination of one or more of the following constituents: CH_2Cl_2, dibasic ester (DBE), n-methylpyrrolidone (NMP), and d-limonene. A CH_2Cl_2-based chemical stripper was used as the standard. The other chemical strippers did not contain CH_2Cl_2. DBE is a mixture consisting of refined dimethyl esters of adipic, glutaric, and succinic acids. The chemical strippers are identified as a number with at least one formulation constituent in parentheses. Individual constituents of each chemical stripper are listed in Table 1.

Coating types included traditional furniture coatings, which are often solvent-based nitrocellulose coatings, and new emerging coating types, which included waterborne and high solids coating types from four major wood furniture coating suppliers. Screening was performed in a laboratory hood at RTI by RTI's laboratory staff. Selected strippers were applied to remove the cured coatings from a 30 cm $\times$ 30 cm area of oak, pine, and maple wood substrates. The manufacturers' directions for the strippers were observed. Coating removal quality achieved by each of the alternative strippers was compared to the removal quality using a CH_2Cl_2-based stripper.

A panel of three non-RTI reviewers qualitatively evaluated the performance of the alternative chemical strippers. Each panelist ranked the quality of coating removal from zero to 10 based upon the percentage of coating removed. A score of 10 represented 100 percent removal while a score of zero represented no activity by the stripper on the coating. The final ranking represented the consensus of the panel. Ranking results are presented in Table 2.

The second objective was to assess the best performing chemical stripper, as found from the laboratory phase, in a furniture repair and refinishing facility. A facility representative applied the stripper and evaluated the quality and ease of coating removal for the alternative stripper selected for on-site assessments. The representative then compared the removal quality and ease of the alternative stripper to the removal quality and ease of the stripper routinely used at the evaluation facility.

RTI personnel estimated the emissions that result from the use of each stripper based upon the quantity of chemical stripper used. Using the information provided by material safety data sheets (MSDSs), RTI personnel estimated VOC and CH_2Cl_2 emissions of the investigated chemical strippers. Emission estimates for the alternative strippers were compared with emission estimates for the currently used products to learn the potential for emission reduction and pollution prevention.

Performance and Materials

The stripping performance of five chemical stripper formulations versus the performance of a CH_2Cl_2-based formulation was measured on furniture quality finished 30 cm × 30 cm solid wood coupons. Wood coupons were prepared according to methods typically used by coating manufacturers to market their coatings to the furniture industry. Three coating types (clear topcoats) from four unnamed coating suppliers were applied to oak, maple, and poplar wood coupons. Of the three wood types, the emphasis of this study was placed on oak. Wood types representation in this study were: porous hardwood, oak; nonporous hardwood, maple; and softwood, poplar. The clear topcoat types were: traditional nitrocellulose lacquer, high-solids, and waterborne coatings. Each of the clear topcoats was applied to the wood substrate using spray and oven curing applications similar to those typically used in a furniture manufacturing facility.

Each wood coupon was treated using a process of three coating steps that consisted of at least a stain, sealer, and clear topcoat. Once received from the coating suppliers the coupons were allowed to cure further for 10 days under ambient conditions. Individual constituents of each chemical stripper used for this test are listed in Table 1.

Application and Removal

All laboratory chemical stripper application and removal tests were conducted under a laboratory hood at approximately 22.4°C (72.3°F). For four cases, the chemical strippers were applied using 2-inch natural bristle brushes following the manufacturer's directions. For the single case where the chemical stripper was not applied using a brush, a heavy paper towel was saturated with the less viscous chemical stripper and applied to the wooden substrate, as the manufacturer suggested.

The area covered by each coating application was approximately 930 cm^2 (1 ft^2). The total coverage area for each of the five chemical strippers was approximately 6.1 m^2 (20 ft^2). The total volume of each chemical stripper used for the total area is presented in Table 3.

Treated coatings were removed with a disposable putty knife that had a blade about 1.3 cm (0.5 in.) wide. Table 4 lists the general ease of removal for the three coating types during the actual removal. Chemical strippers are identified above each column, and the coating types are listed beside each row in Table 4. Once the coatings were removed from the wooden coupons with the putty knife, the surface was wiped with a cloth and received no further treatment.

Stripper Evaluation

Laboratory Evaluation. Following stripper application and removal, a panel of individuals experienced in the area of chemical stripping visually evaluated the performance effectiveness of each chemical stripper on each coating type. Each chemical stripper test was ranked on a scale from zero to 10 (where, zero represented no activity by the stripper to remove the coating, and 10 represented 100 percent coating removal). The ranking results of the visual evaluation are presented in Table 2.

Figures 1 and 2 are photos of the test coupons with coatings removed using Chemical Stripper 4 (d-Limonene) and Chemical Stripper 5 (H_2O), respectively. Below each photo is the chemical stripper used in the screening evaluation. The chemical strippers ranked in order of best to worst are: Chemical Stripper 4 (d-Limonene), Chemical Stripper 5 (H_2O), Chemical Stripper 3 (NMP, DBE), Chemical Stripper 1 (Standard), and Chemical Stripper 2 (NMP, DBE). The top three performing chemical strippers from this study were closely ranked, Chemical Stripper 4 (d-Limonene) at 7.9, Chemical Stripper 5 (H_2O) at 7.5, and Chemical Stripper 3 (NMP, DBE) at 7.3. According to the panel, Chemical Stripper 4 (d-Limonene) was the most effective chemical stripper in the group. Figures 3 and 4 are photos of test coupons with coatings removed using Chemical Stripper 4 (d-Limonene). Because of its low vapor pressure, chemical stripper 5 (H_2O) can be left on the paint for extended periods without loss of solvents, allowing more flexibility in working time. However, this DBE chemical stripper is waterborne and can raise the grain of wooden substrates. Material cost for chemical strippers at the time of this study is presented in Table 5. The relative cost of the chemical strippers for the area treated in this study is listed in Table 6.

Furniture Repair and Refinishing Facility Evaluation. A local refinisher demonstrated the stripping effectiveness of Chemical Stripper 4 (d-Limonene) in his facility on a chair seat, a square table top, and circular table top. The participating refinisher was not aware of the specific coating types on the substrates; however, he took the liberty to speculate on the general coating type based on appearance, removal ease, and his experience. The coatings removed from the square table surface consisted of several layers of paint covering the original varnished surface with a removal time of approximately 45 minutes. Coatings removed from the chair seat were layers of lacquer-type finishes with a removal time of approximately 10 minutes. Removal time for coatings removed from the circular table top was approximately 6 minutes, and the coatings removed consisted of a traditional lacquer furniture coating system. All furniture pieces were presumed to have been solid wood. The area of coating removed was roughly 930 cm^2 (1 ft^2) from each surface.

Chemical Stripper 4 (d-Limonene) successfully removed the topcoats from the lacquer-type surfaces of the chair and circular table top without disturbing the appearance of the stain. However, it left a film on the lacquer-type surface that was removed by wiping the surface with an unsoiled cloth moistened with Chemical Stripper 4 (d-Limonene). Roughly three layers of paint and one layer of varnish were removed from the square table top leaving a raw wood surface. The refinisher said that the product was reliable. However, he was concerned with the cost.

Conclusions

Results from this evaluation included: (1) the subjective determination of a viable substitute for solvent-based chemical strippers based upon the effectiveness of the evaluated alternative chemical strippers, (2) the potential effect of the alternative chemical stripper on air emissions, and (3) the cost associated with the use of the alternative chemical stripper. Implementing the use of the alternative chemical stripper as a viable substitute was at the discretion of the host facility.

The VOC and CH_2Cl_2 emission estimates resulting from the use of alternative chemical strippers and currently used solvent-based chemical strippers were calculated using the available information provided from the MSDSs of each chemical and the amount of chemical stripper used. A cost assessment was generated from usage information provided by the host facility and cost information provided by the vendor for chemical strippers only. Relative costs and emission estimates are presented in Tables 6 and 7, respectively. Waste management, other cost associated with using the alternative chemical stripper, and handling and safety were not directly related to the objectives of this study and should be included in future work.

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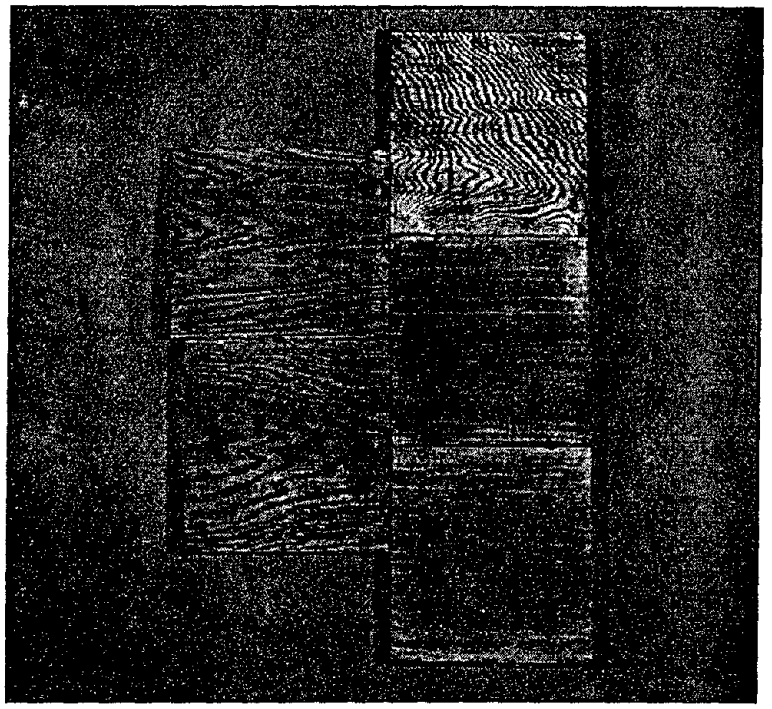

FIGURE 1. PHOTO OF TEST COUPONS FINISHED WITH VARIOUS FURNITURE COATINGS AND THEN STRIPPED USING CHEMICAL STRIPPER 4 (D-LIMONENE).[1]

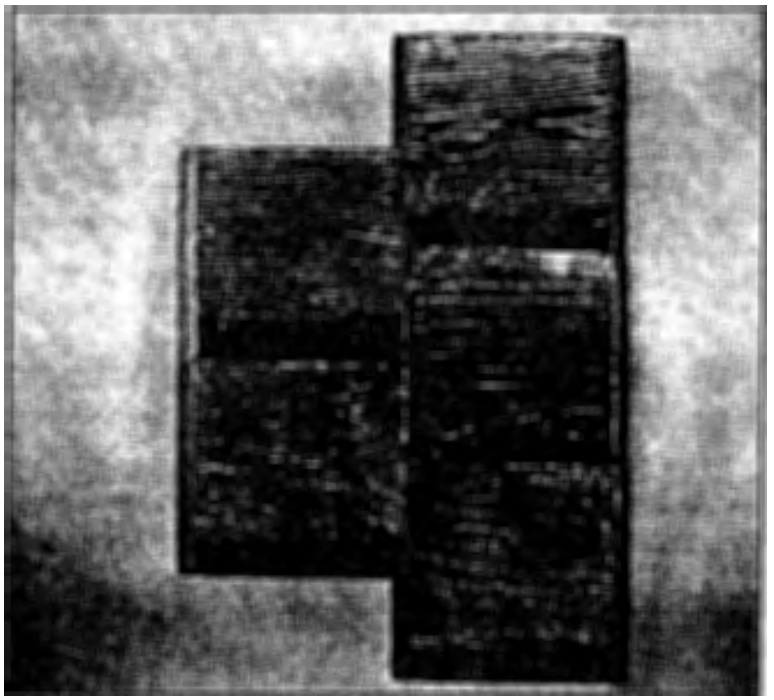

FIGURE 2. PHOTO OF TEST COUPONS FINISHED WITH VARIOUS FURNITURE COATINGS AND STRIPPED USING CHEMICAL STRIPPER 5 (H_2O).[1]

1 Coatings and wood types from top-to-bottom and left-to-right in figure are: waterborne on oak, high-solids on oak, and nitrocellulose lacquer on oak, poplar, and maple.

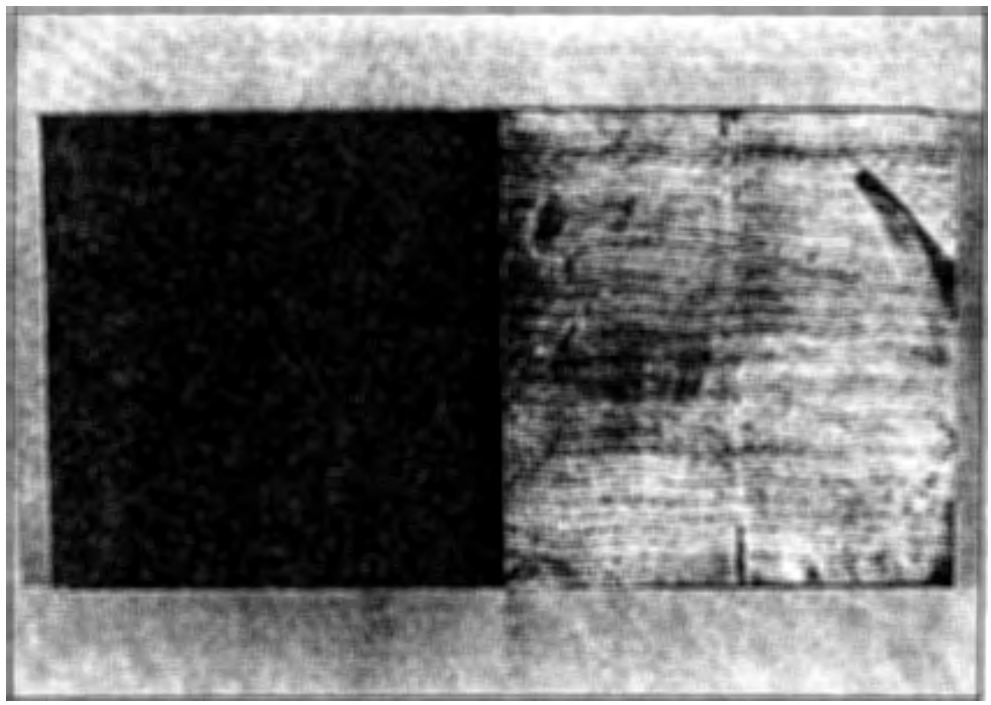

FIGURE 3. PHOTO OF TEST COUPONS FINISHED WITH A LACQUER SYSTEM ON MAPLE BEFORE AMD AFTER TREATMEMT USING CHEMICAL STRIPPER 4 (D-LIMONENE).

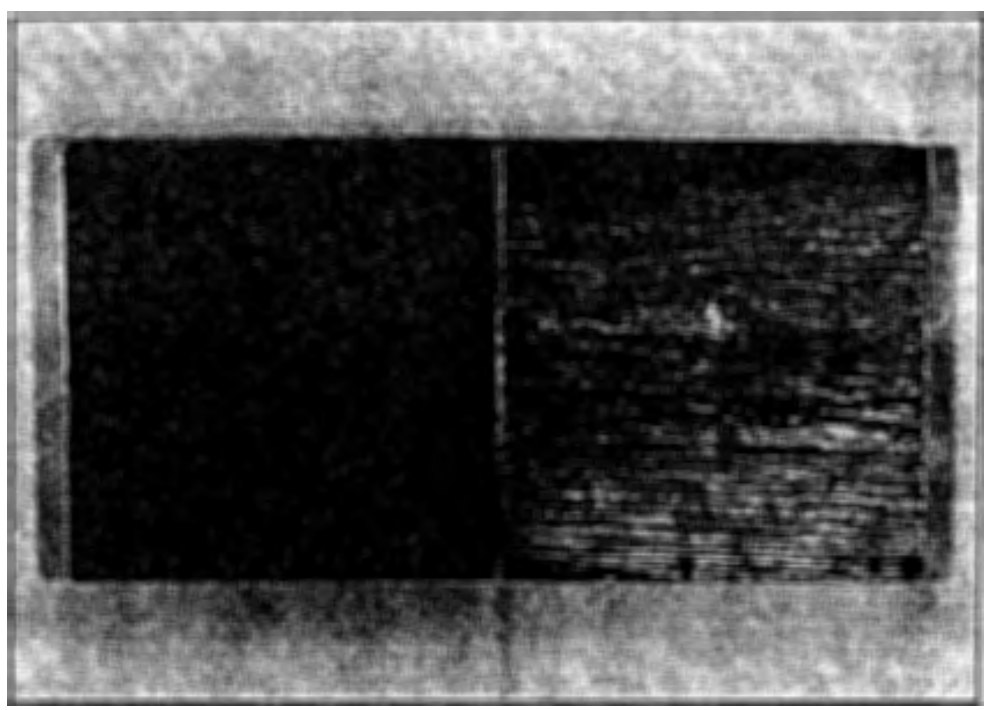

FIGURE 4. PHOTO OF TEST COUPONS FINISHED WITH A HIGH-SOLIDS SYSTEM ON OAK BEFORE AND AFTER TREATMENT USING CHEMICAL STRIPPER 4 (D-LIMONENE).

TABLE 1. CONSTITUENTS OF CHEMICAL STRIPPERS

CHEMICAL STRIPPER	CONSTITUENT	WEIGHT %
1 (Standard)	Methylene Chloride *	> 10
	Methanol *	< 25
	Toluene *	> 35
	Acetone	< 25
	Paraffin Wax	< 5
2 (NMP, DBE)	N-Methyl-2-Pyrrolidone	†
	Dimethyl Glutarate	†
	Dimethyl Adipate	†
	Dimethyl Succinate	†
3 (NMP, DBE)	1-Methyl-2-Pyrrolidone	†
	Dimethyl Glutarate	†
	Dimethyl Adipate	†
	Dimethyl Succinate	†
4 (d-Limonene)	n-Methyl Pyrrolidone	50 - 75
	d-Limonene	25 - 50
5 (H_2O)	Water	65 - 75
	Dimethyl Adipate	20 - 30
	Dimethyl Glutarate	1 - 5
	Hydrated Magnesium Aluminum Silicate	0 - 2
	Hydrated Aluminosilicate	0 - 2

* Hazardous Air Pollutants

† Constituent weight percent undisclosed on Material Safety Data Sheets (MSDSs); therefore, primary constituent can not be identified.

TABLE 2. AVERAGE RANKING FROM STRIPPING EVALUATIONS *

	1 (Standard)	2 (NMP, DBE)	3 (NMP, DBE)	4 (d-Limonene)	5 (H_2O)
Panelist 1	5.6	3.9	6.8	8.0	7.9
Panelist 2	7.6	6.2	8.1	8.2	8.0
Panelist 3	4.3	4.0	7.1	7.4	6.8
Average	5.8	4.7	7.3	7.9	7.5

* All significant figures are not shown. Numbers are rounded to the nearest one hundredth.

TABLE 3. USAGE ESTIMATES

CHEMICAL STRIPPER	VOLUME/COVERAGE AREA, (m^3/m^2)
1 (Standard)	1.22×10^{-4}
2 (NMP, DBE)	1.74×10^{-4}
3 (NMP, DBE)	2.67×10^{-4}
4 (d-Limonene)	3.23×10^{-4}
5 (H_2O)	6.47×10^{-4}

TABLE 4. REMOVAL EASE FOR COATINGS

Coating Types	1 (Standard)	2 (NMP, DBE)	3 (NMP, DBE)	4 (d-Limonene)	5 (H_2O)
Nitrocellulose	VE	VE	VE	VE	VE
Waterborne	RE	RE	RE	D	RE
High Solids	RE	RE	RE	D	VE

VE = VERY EASY RE = RELATIVELY EASY D = DIFFICULT

TABLE 5. MATERIAL COST (U.S. DOLLARS)

CHEMICAL STRIPPER	QUART	GALLON
1 (Standard)	4.03	10.17
2 (NMP, DBE)	7.95	21.94
3 (NMP, DBE)	9.22	25.16
5 (H_2O)	6.79	16.37
4 (d-Limonene)	11.73*	46.93*
	9.73†	38.93†

* 4 (d-Limonene) is only available for purchase in 5- and 55-gallon quantities, this is an estimate using the 5-gallon quantity.

† 4 (d-Limonene) is only available for purchase in 5- and 55-gallon quantities, this is an estimate using the 55-gallon quantity.

TABLE 6. RELATIVE MATERIAL COST FOR STRIPPING A FIXED AREA ** (U.S. DOLLARS)

CHEMICAL STRIPPER	COST/AREA, ($/m^2)	RELATIVE COST
1 (Standard)	0.52	1.0
2 (NMP, DBE)	1.46	2.8
3 (NMP, DBE)	2.61	5.0
5 (H_2O)	4.65	9.0
4 (d-Limonene)	3.40†	6.6†
	2.82*	5.4*

* All significant figures are not shown. Numbers are rounded to the nearest one hundredth.

† 4 (d-Limonene) is only available for purchase in 5- and 55-gallon quantities, this is an estimate using the 5-gallon quantity.

* * 4 (d-Limonene) is only available for purchase in 5- and 55-gallon quantities, this is an estimate using the 55-gallon quantity.

TABLE 7. EMISSION ESTIMATES

CHEMICAL STRIPPER	VOC	CH_2Cl_2
	MASS/AREA, (g/m^2)	
1 (Standard)	85.85	9.54
2 (NMP, DBE)	160.90	-
3 (NMP, DBE)	263.74	-
4 (d-Limonene)	158.94	-
5 (H_2O)	139.86	-

SESSION 8A

MILITARY APPLICATIONS

PAPERS PRESENTED:

"Low- and No-VOC Conformal Coatings Over No-clean Flux Residues"
by
Edward Shearls
SAIC
Indianapolis, Indiana

"Low-VOC and No-VOC Coating Systems for Aerospace and Its Support"
by

Dan Bernard
DEFT, Inc.
Irvine, California

"Low VOC Marine Coatings"
by
Charles Ayers
Jotun/Valspar
Baltimore, Maryland

"Evaluate Alternative Paint Stripping Technologies Used in Aircraft and Space Vehicles"
by
Geddes Ramsey
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, North Carolina

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

LOW- AND NO-VOC CONFORMAL COATINGS OVER NO-CLEAN FLUX RESIDUES

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INTRODUCTION

The use of conformal coatings over Printed Wiring Assemblies (PWAs) today presents three manufacturing challenges. First, in response to the impending phaseout of chlorofluorocarbon-based solvents, low residue or no-clean fluxes have been developed. These fluxes are advertized as leaving no, or very little benign residue after the soldering process, but the main concern is whether these benign residues interfere with conformal coating adhesion to PWAs. Second, most conformal coatings in use release significant amounts of volatile organic compounds (VOCs) during coating application. The use of new conformal coatings with lower VOC content and less environmental impact is rapidly becoming an important issue. The Clean Air Act of 1990 drives the eventual use of no- or low-VOC conformal coatings with negligible environmental impact. The third challenge is to determine whether it is feasible and practical to apply a low-VOC coating over a no-clean flux.

This paper describes results of a three phase effort that addresses these challenges completed at the Electronics Manufacturing Productivity Facility (EMPF). Phase 1 evaluated the adhesion and performance of current (not low-VOC) acrylic, polyurethane, silicone, and parylene conformal coatings applied over test pallets manufactured with no-clean (low residue) fluxes and pastes. Phase 2 evaluated the use of currently available low-VOC conformal coatings applied over commonly used RMA and water soluble fluxes and pastes. Environmental stress screening (ESS) tests were performed in both phases to down select no-clean materials and low-VOC coatings for further testing in Phase 3, the application of low-VOC coatings over no-clean fluxes and pastes on functional boards (PWAs).

METHODOLOGY

Preliminary Compatibility Testing

Preliminary compatibility testing was performed to ensure test pallet (Phase 1 and 2) and functional test board (Phase 3) base materials (fluxes, pastes, base metals, laminate, and solder mask combinations) were compatible. Five RMA fluxes, four water-soluble fluxes, seven RMA pastes, and six water-soluble pastes comprised the matrix of representative common fluxes and pastes tested. A popular liquid photoimageable (LPI) and a popular dry film solder mask were tested.

Fluxes were applied to test pallets using individual spray bottles. Pastes were printed using an 80-mesh, 10-mil-thick screen. Pallets were wave soldered or IR reflowed according to manufacturers' technical literature. Those made with RMA materials were cleaned with 10% Armakleen E-2001 detergent. Those made with water-soluble materials were cleaned with DI water only. The flux and

paste producing the best soldered pallets were used to make Phase 2 test pallets and Phase 3 PWAs.

Test Pallets and Coupons

The test pallets used in the Phase 1 and Phase 2 efforts were 4.00 inches by 5.00 inches (10.20 x 12.75 cm) and had four test coupons to a pallet, with break-away tabs between the coupons (see Figure 1). Each test coupon contained a 1.00 inch by 1.50 inch (2.54 x 3.80 cm) copper rectangle with a 0.50 inch by 1.00 inch (1.27 x 2.54 cm) solder mask strip down the center. One half of the test pallets had coupons with LPI film solder mask, the other half had dry film solder mask. The majority of the coupons had bare copper on the areas adjacent to the solder mask. The remainder had hot air solder leveled (HASL) on the areas adjacent to the solder mask. The laminate was FR4 material.

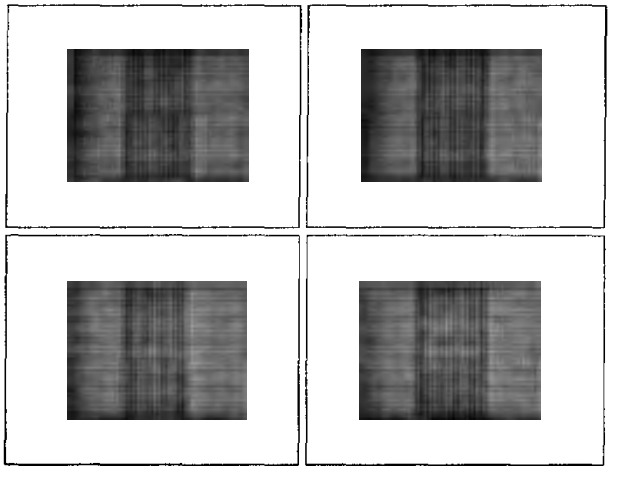

Figure 1 Test Coupon

The masks and the metal surfaces allowed the base metal/mask test coupon combinations:

- Copper/Photoimageable Liquid
- Copper/Dry Film
- HASL/Photoimageable Liquid
- HASL/Dry Film

Including the FR4, this arrangement allowed evaluation of conformal coating adhesion to five different substrates and interfaces after application of the various flux residues.

Phase 1. No-Clean Flux Evaluation

It was impossible to evaluate every standard (not low-VOC) conformal coating and no-clean flux. One acrylic, one polyurethane, one silicone and one parylene were randomly selected to represent their respective coating families. The coatings were applied at Specialty Coating Services of Indianapolis, Indiana. Flux and paste selection were more complicated because of the broadness of the no-clean definition. The materials available were grouped into resin, rosin, or rosin/resin free categories, and further divided by solids content, activator and carrier. Twelve pastes and eleven fluxes were chosen to represent the no-clean industry.

Liquid fluxes were applied to the test pallets with a high pressure spray system designed for no-clean fluxes. Precision Dispensing Equipment of Bay Village, Ohio brought the system to the EMPF and operated it. The fluxes were processed on a nitrogen inerted wave soldering machine using a profile recommended by material vendors. No-clean solder pastes were printed to the test pallets and reflowed in a nitrogen environment using forced convective air reflow and a profile recommended by the material vendor.

In Phases 1 and 2, representative pieces of the conformal coated coupons were visually examined and tested for adhesion. Additional samples were subjected to ESS tests which included either temperature/humidity, thermal cycle, thermal shock, salt fog, a sequence of all tests, or no test. The stress tests and conditions used are listed in Table 1.

TABLE 1 ENVIRONMENTAL SCREENING TEST SUMMARY		
Stress Test	Specification	Conditions
Temperature/Humidity	MIL-STD-810D Method 507.2	168 hours, 30 to 60° C; 85-95% relative humidity
Thermal Cycling	IPC-TM-650 Method 2.6.6	24 hours, -55 to +125° C; 30 min per temp and 15 min dwell at 25° C between each ramp
Thermal Shock	MIL-STD-202F Method 107D	24 hours, -55 to +125° C; 15 min per temp.
Salt/Fog	MIL-STD-810D Method 509.2	48 hours, 35° C

ASTM D3359 was used to measure conformal coating adhesion, modified to eliminate as much of the subjectivity as possible. Instead of a hand-held cutting tool, an IBM robot was fitted to hold the cutting tool and the test coupon and programmed to perform the actual cutting. The coupon was cut and then rotated 90 degrees and cut again to form a lattice pattern. A specified tape was pressed over the area and then removed. Use of the robot gave uniform depth, pressure and lattice formations. The same technician performed all tape applications and ratings. Adhesion was rated for each substrate on a 5 to 0 point system, with 5 best and 0 worst as shown in Table 2.

TABLE 2 ADHESION GRADING SCHEME	
GRADE	CRITERIA
5	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
4	Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
3	Small flakes of the coating are detached along the edges and at intersections of cuts. The area is 5-15% of the lattice.
2	Coating has flaked along the edges and on parts of the squares. The area affected is 15-35% of the lattice.
1	Coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35-65% of the lattice.
0	Flaking and detachment worse than grade 1.

Phase 2. Low-VOC Conformal Coating Evaluation

The most compatible RMA and water soluble fluxes and pastes, determined by preliminary compatibility testing, were used to make test pallets as described in that section for low-VOC conformal coating evaluation. Fourteen different conformal coatings representing the generic coating groups were applied to test pallet replicates (ten of each type shown in Table 3).

TABLE 3. TEST PALLET MATRIX

Solder Mask	Flux		Paste	
	RMA	Water Soluble	RMA	Water Soluble
Liquid Film	X	X	X	X
Dry Film	X	X	X	X

After a literature review, it was decided that LPI solder mask pallet results were the primary criteria for flux, paste, and conformal coating selections in this project, as LPI solder mask would be used on the pallets for the Phase 3 (no-clean materials with low-VOC conformal coatings) effort. LPI solder mask has been shown the most compatible with no-clean fluxes[1] and more compatible with conformal coats than other types[2]. A solder mask comparison[3] reports LPI masks reduce tombstoning and solder balls, withstand multiple reflow cycles, and are easily cleaned. Several papers describe favorable solder ball dynamics with LPI masks [4,5,6,7].

The coatings were evaluated using the environmental screening tests described earlier to determine the most promising one from each generic group to use in the Phase 3 effort.

Phase 3. Low-VOC Conformal Coating Over No-Clean Flux Evaluation

Populated boards (PWAs) were manufactured for the Phase 3 evaluation using the liquid film photoimageable solder mask and the laminate from earlier testing. The no-clean fluxes and pastes that graded best in the Phase 1 effort was used for one set of these boards. The RMA fluxes and pastes and the water soluble fluxes and pastes selected in the compatibility pretesting were used to manufacture two additional sets of populated boards. A set of not-populated boards served as a final control set.

The RMA and water soluble paste and flux combinations representing current industry conditions and the no-clean fluxes and pastes used in the Phase 3 effort are shown in Table 4. These fluxes and pastes demonstrated the best adhesion with the traditional conformal coatings on the test coupons.

The low-VOC conformal coatings chosen for Phase 3 are shown in Table 5. These conformal coatings demonstrated the best adhesion when used with traditionally fluxed and cleaned test coupons.

Table 6 shows the ESS test fate for each board in a 12 replicate set. One board in each group was not ESS tested.

TABLE 4 FLUX & PASTE SELECTION		
	PASTE	FLUX
RMA	Alpha RMA 209	Alpha 615 RMA
WS	Amtech WS-465XT	Lonco Organo Flux 3355 VF
No-Clean	AIM LR5 AIM Base I	Alpha 970S Kester 970S Hi-Grade 3570-T Alpha NR200

TABLE 5 CONFORMAL COATING SELECTED	
Conformal Coating Type	Conformal Coating Selected
Acrylic	Quick Cure 576
Urethane	Dymax 986
Epoxy	Envibar 1244T
Silicone	Loctite 5290
Parylene	Parylene C

TABLE 6 BOARD TESTING SCHEME	
BOARD NUMBER	ESS TEST
1-3	SIR
4-6	Sequential ESS
7	No ESS
8	Humidity Only
9	Thermal Cycle Only
10	Thermal Shock Only
11	Salt Fog Only
12	Spare PWA

PWAs were visually examined and tested for adhesion in four different locations, (two on the top-side and two on the bottom-side). The slightly modified version of ASTM D3359 described earlier was used to measure conformal coating adhesion. Adhesion was rated using the grading system shown in Table 2.

RESULTS

Visual Inspection of Conformal Coatings

Visual Inspection Of Acrylic Coating

Control PWAs (non-populated PWAs) had minor dewetting on both sides and some coating discoloration. Major dewetting occurred on the component side of all processed (fluxed) assemblies, and the Plastic Leaded Chip Carriers (PLCCs) and other chips. PWAs manufactured with RMA and no-clean paste and flux also showed poor adhesion of the conformal coating on the PLCCs after being environmentally stressed. Lighter colored PLCC areas could be flaked easily using a probe or a fingernail. Acrylic coatings on the no-clean assemblies were discolored and were "bubbled" on the bottom side. PWAs made with water soluble flux and paste had good, uniform coating coverage on their bottom sides.

Visual Inspection Of Polyurethane Coating

Minor dewetting on the PLCCs and chips occurred on the boards made with RMA and no-clean paste and flux. The no-clean paste and flux displayed dewetting around the component pad areas. Control PWAs and PWAs manufactured with water soluble paste and flux displayed coatings with good, uniform coverage.

Visual Inspection Of Parylene Coating

All PWAs displayed good, uniform Parylene coatings.

Visual Inspection Of Epoxy Coating

The coating on all PWAs displayed major dewetting on the component side and the PLCCs and chips. The PLCCs exhibited adhesion problems after environmentally stressing. PWAs manufactured with RMA or water soluble paste and flux displayed good, uniform Epoxy coatings on their bottom sides. PWAs manufactured with no-clean paste had slight dewetting on their bottom sides.

Visual Inspection Of Silicone Coating

Control PWAs and all PWAs manufactured with RMA or water soluble paste and flux produced Silicone coatings with good, uniform coverage. PWAs manufactured with no-clean paste and flux displayed slight dewetting around component pad areas.

Adhesion of Conformal Coatings After Environmental Stress Testing

The top and bottom board adhesions for each PWA were rated on a 0-5 scale, then converted to a percent (100 percent maximum). Table 7 shows the overall average adhesion by coating for each ESS test. Table 8 shows the average percent adhesion for each coating as a function of the paste/flux type for each ESS test.

Adhesion of Acrylic Coating after ESS

The PWAs that went through only Humidity and only Salt Fog tests had average adhesions of 25 percent (see Table 7). No paste/flux material did well but values for boards made with no-clean materials were exceptionally poor (see Table 8). PWAs that went through all environmental stresses had an average adhesion of 55 percent, again because of poor adhesion for no-clean material boards. PWAs that saw no environmental stresses had an average adhesion of 61 percent. Thermal shock and thermal cycling tests, with resultant average adhesions of 86 and 90 percent respectively, had the least effects on PWA adhesion.

Analyzed in overall terms of paste/flux materials (see Table 8), the acrylic coated PWAs made with RMA and the water soluble paste and flux had adhesion averages of 64 and 62 percent, respectively. The control PWAs had an average adhesion of 65 percent. The no-clean paste and flux had the lowest adhesion average (37 percent).

TABLE 7 AVERAGE ADHESION BY ESS TEST vs COATING TYPE

	ESS TEST					
COATING	HUMID	T.CYCLE	T.SHOCK	SALT FOG	ALL	NONE
ACRYLIC	25	90	86	25	55	61
URETHANE	69	78	79	78	71	75
PARYLENE	99	90	85	80	96	98
EPOXY	91	89	86	50	80	86
SILICONE	69	64	61	65	74	80
average	71	82	81	61	81	80

Adhesion of Urethane Coating after ESS

Urethane coatings produced boards with average adhesions from 69 to 79 percent (Table 7). The PWAs that went through humidity stress only had an average adhesion of 69 percent. PWAs that went through all environmental stresses had an average adhesion of 71 percent. PWAs that saw no environmental stresses had an average adhesion of 75 percent. PWAs that went through only thermal cycling, or thermal shock, or salt fog, had average adhesions of 78 or 79 percent.

In terms of paste/flux materials (Table 8), average adhesions ranged from 69 to 80 percent. The control PWAs had an average adhesion of 69 percent. The PWAs manufactured with RMA paste and flux had an average adhesion of 80 percent. The PWAs manufactured with water soluble paste and flux had an average adhesion of 77 percent. The PWAs manufactured with no-clean paste and flux had an average adhesion of 73 percent.

Adhesion of Parylene Coating after ESS

The average salt fog adhesion value of 80 percent (Table 7) for PWAs coated with Parylene is a reflection of the poor adhesion (30 percent average) on PWAs made with RMA (Table 8). Parylene coated PWAs that went through only thermal shock testing had an average adhesion of 85 percent.

PWAs that went through only thermal cycling had an average adhesion of 90 percent. PWAs that saw no environmental stresses had an average adhesion of 98 percent. PWAs that went through humidity and PWAs that saw all environmental stresses had average adhesions of 99 and 96 percent, respectively.

In terms of paste/flux materials (Table 8), the control PWAs had the best adhesion (99 percent), followed by PWAs manufactured with water soluble paste and flux (93 percent average adhesion). PWAs manufactured with RMA paste and flux had average adhesion of 87 percent. The PWAs manufactured with low-residue paste and flux had a comparable adhesion of 84 percent.

Adhesion of Epoxy Coating after ESS

The epoxy coated PWAs that went through only salt fog testing had an average adhesion of 50 percent (Table 7), again because of the poor adhesion of the boards made with no-clean materials (Table 8). PWAs that went through all environmental stresses had an average adhesion of 80 percent. The remaining ESS tests produced adhesion values that were essentially equivalent. PWAs that saw no environmental stresses and the PWAs that went through only thermal shock had average adhesions of 86 percent. PWAs that went through only thermal cycling had an average adhesion of 89 percent. Individual humidity testing produced an average adhesion of 91 percent.

In overall terms of paste/flux materials (Table 8), the control PWAs had the best average adhesion value (95 percent). The RMA paste and flux PWAs had an average adhesion of 86 percent. The water soluble paste and flux had an average adhesion of 82 percent. The no-clean paste and flux had average adhesion of 58 percent.

Adhesion of Silicone Coating after ESS

The silicone coated PWAs generally did poorly in the various individual ESS tests, with average adhesion values in the 61 to 69 percent range (Table 7). PWAs that saw all environmental stresses had an average adhesion of 74 percent. The PWAs that saw no environmental stresses had average adhesion of 80 percent.

In terms of paste/flux materials (Table 8), the PWAs manufactured with water soluble paste and flux had an average adhesion of 74 percent. Those manufactured with RMA paste and flux and the control PWAs had average adhesions of 71 and 70 percent, respectively. The PWAs manufactured with no-clean paste and flux had an average adhesion of 60 percent.

Overview Of Conformal Coating Adhesion

In terms of severity for the conformal coatings tested (Table 7), the salt fog test is most severe with an average adhesion of 61 percent. Humidity testing produces an average adhesion of 71 percent. The remaining ESS tests are equivalent in severity, with average adhesions of 81 or 82 percent. Control PWA adhesion is 80 percent.

When all environmental stresses are averaged for the various paste and flux combinations (Table 9), the PWAs coated with Parylene C had the highest average adhesion (91 percent). PWAs coated with epoxy were next with an average of 80 percent adhesion. The urethane coated boards had 75 percent average adhesion, followed by silicone-coated PWAs with 69 percent average adhesion and acrylic-coated PWAs with 57 percent average adhesion.

TABLE 8 ADHESION MATRIX					
COATING & TEST	PASTE/FLUX TYPE				
ACRYLIC	RMA	WATER SOLUBLE	NO-CLEAN	CONTROL	ESS AVE
HUMIDITY	35	40	0	25	25
THERMAL CYCLE	85	100	75	100	90
THERMAL SHOCK	90	70	85	100	86
SALT FOG	25	50	0	25	25
ALL	72	60	15	72	55
NONE	80	50	45	70	61
paste/flux ave	64	62	37	65	57
URETHANE					
HUMIDITY	80	60	75	60	69
THERMAL CYCLE	80	80	70	80	78
THERMAL SHOCK	80	80	75	80	79
SALT FOG	80	80	75	80	78
ALL	78	90	69	46	71
NONE	80	75	75	70	75
paste/flux ave	80	78	73	69	75
EPOXY					
HUMIDITY	100	100	65	100	91
THERMAL CYCLE	90	90	75	100	89
THERMAL SHOCK	80	90	75	100	86
SALT FOG	70	45	5	80	50
ALL	89	92	40	88	77
NONE	85	75	85	100	86
paste/flux ave	86	82	58	95	80
SILICONE					
HUMIDITY	70	80	65	60	69
THERMAL CYCLE	60	70	65	60	64
THERMAL SHOCK	60	60	65	60	61
SALT FOG	75	75	30	80	65
ALL	80	77	58	80	74
NONE	80	80	80	80	80
paste/flux ave	71	74	60	70	69
PARYLENE					
HUMIDITY	100	100	95	100	99
THERMAL CYCLE	100	80	80	100	90
THERMAL SHOCK	95	80	65	100	85
SALT FOG	30	100	90	100	80
ALL	98	100	84	100	96
NONE	100	100	95	95	98
paste/flux ave	87	93	84	99	91

TABLE 9 ADHESION MATRIX AVERAGES					
COATING & TEST	PASTE/FLUX TYPE				
COATING	RMA	WATER SOLUBLE	NO-CLEAN	CONTROL	ESS AVE
ACRYLIC	64	62	37	65	57
URETHANE	80	78	73	69	75
EPOXY	86	82	58	95	80
SILICONE	71	74	60	70	69
PARYLENE	87	93	84	99	91

SIR Testing

SIR values are shown in Table 10 and Figures 2-6. None of the SIR value changes shown are significant value changes and none would be classed a failure. Average SIR values improved after SIR testing for the epoxy, silicone, and urethane coatings. Average SIR values decreased slightly (0.44 log ohm; less than one order of magnitude) for the acrylic coating and decreased even more (1.19 log ohm; slightly over one order of magnitude) for the Parylene coating. The average SIR value for the parylene group is almost 2 log ohms less than that of the closest group (the acrylic coating). Note that for all but the silicone group, the No-clean boards had the lowest SIR values in each group (Figures 2-6). The No-clean boards had a higher SIR value than the RMA and Control Boards in the silicone coating group.

Figure 7 shows average adhesion values for the five conformal coatings evaluated in the Phase 3 effort plotted for the RMA, Water-soluble, and No-clean fluxes and pastes used to manufacture the PWAs. The flux/paste graph lines are relatively close together over the urethane, silicone, and parylene conformal coatings, indicating all have equivalent adhesion for the materials tested.

CONCLUSIONS

A viable test vehicle (pallet) and methodology for assessing interactions between no-clean materials and low-VOC conformal coatings have been developed.

The results of this effort indicate that it is practical to use low-VOC coatings over no-clean fluxes and pastes in some circumstances. When materials are graphed against adhesion (Figure 7), it is apparent that the urethane, silicone, and parylene conformal coatings used in this study have as good adhesion over no-clean materials as over RMA and water-soluble materials.

It is important to remember these results apply only to the specific coatings tested and the specific fluxes, pastes, and solder mask over which they were applied. Coatings that did not perform well in these tests will perform very well with different PWA materials. Coating performance is related to material compatibility. It is extremely important that all materials be carefully screened for compatibility before selecting a no-clean flux/paste and low-VOC conformal coating combination. It is also important to fine tune manufacturing processes employed and then keep them constant. Small process changes can have large effects on surface conditions, which in turn effect conformal coating adhesion.

All reports and data analysis for each phase effort and the initial compatibility testing are available from the EMPF library.

TABLE 10 SIR VALUES (LOG OHMS)					
ACRYLIC COATING	INITIAL	24 HRS	96 HRS	168 HRS	FINAL
RMA	11.71	8.50	8.38	8.46	12.01
WATER SOLUBLE	11.57	8.39	8.31	8.38	11.55
NO-CLEAN	12.61	7.69	7.93	8.12	10.90
CONTROL BOARD	12.19	8.17	8.34	8.46	11.87
average	12.02				11.58
EPOXY COATING	INITIAL	24 HRS	96 HRS	168 HRS	FINAL
RMA	10.77	8.35	8.43	7.89	12.40
WATER SOLUBLE	10.65	**	8.33	7.81	12.23
NO-CLEAN	10.82	**	8.11	8.69	11.58
CONTROL BOARD	10.82	**	8.35	8.03	12.06
average	10.76				12.07
PARYLENE COATING	INITIAL	24 HRS	96 HRS	168 HRS	FINAL
RMA	10.80	8.56	8.19	8.11	9.76
WATER SOLUBLE	10.84	8.51	8.28	8.16	10.21
NO-CLEAN	10.41	7.83	7.66	7.59	8.88
CONTROL BOARD	11.07	8.28	8.11	8.01	9.50
average	10.78				9.59
SILICONE COATING	INITIAL	24 HRS	96 HRS	168 HRS	FINAL
RMA	11.50	8.51	8.35	8.26	12.03
WATER SOLUBLE	11.34	**	8.51	8.45	12.53
NO-CLEAN	11.90	**	8.42	8.32	12.27
CONTROL BOARD	11.27	**	8.23	8.07	11.86
average	11.50				12.17
URETHANE COATING	INITIAL	24 HRS	96 HRS	168 HRS	FINAL
RMA	11.04	8.00	8.14	7.82	12.34
WATER SOLUBLE	10.98	7.87	7.94	7.82	12.39
NO-CLEAN	10.84	7.72	7.94	8.11	11.38
CONTROL BOARD	10.80	7.58	7.82	7.93	11.95
average	10.91				12.01

** Data lost through equipment malfunction

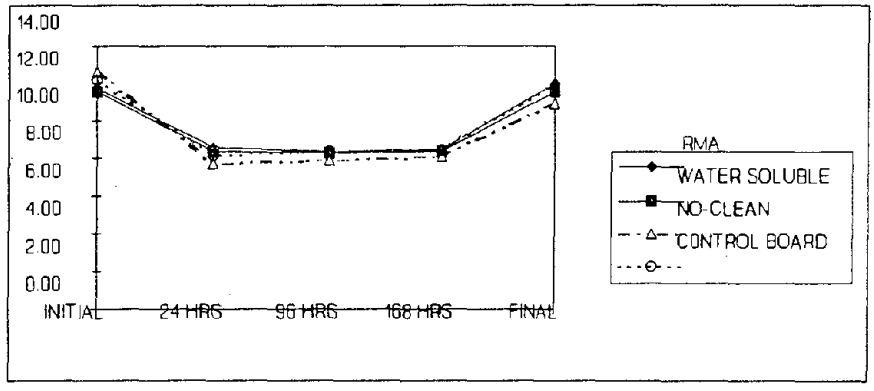

FIGURE 2 ACRYLIC COATING SIR VALUES

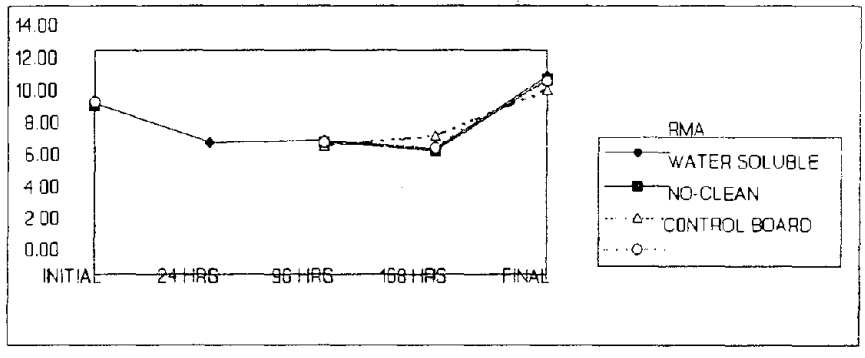

FIGURE 3 EPOXY COATING SIR VALUES

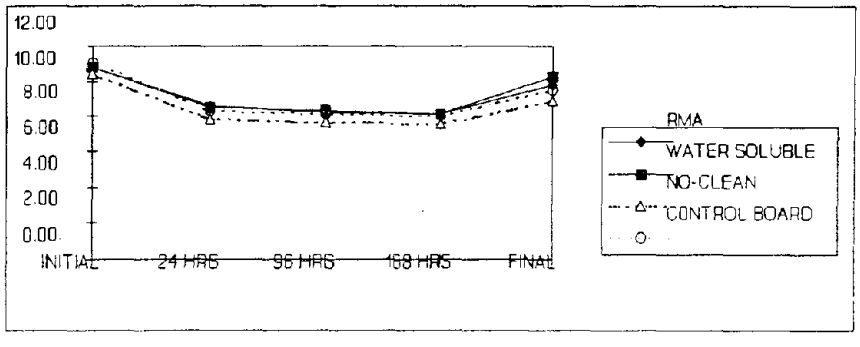

FIGURE 4 PARYLENE COATING SIR VALUES

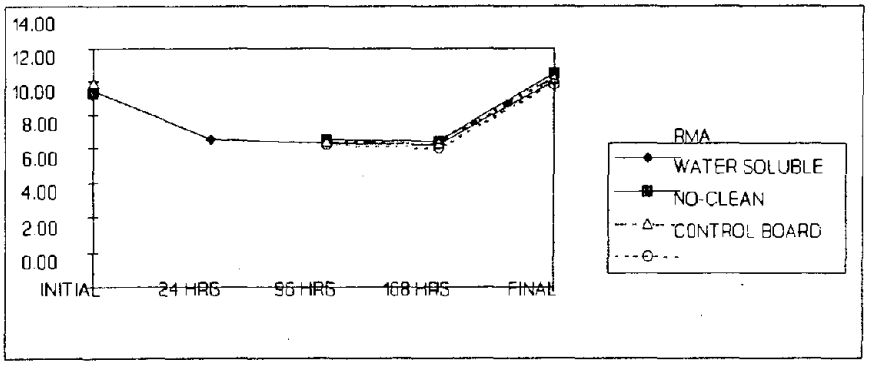

FIGURE 5 SILICONE COATING SIR VALUES

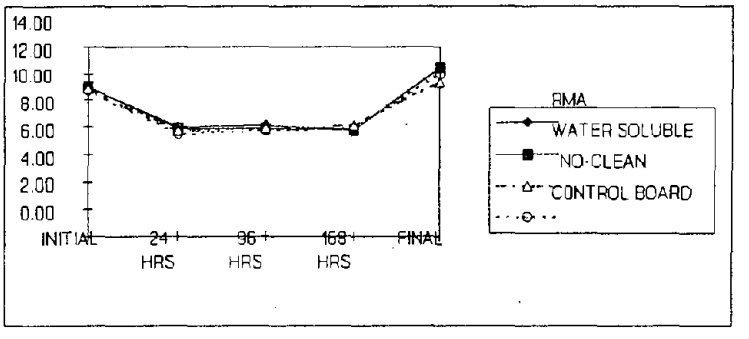

FIGURE 6 URETHANE COATING SIR VALUES

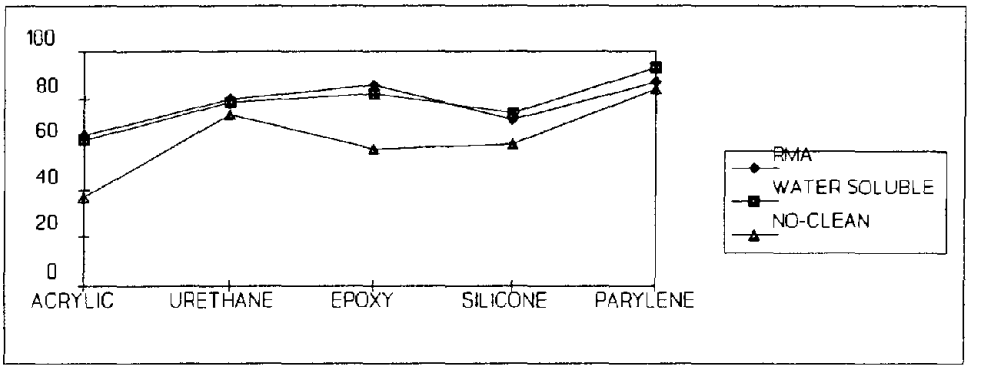

FIGURE 7 MATERIAL COMPARISON

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Low VOC and No-VOC Coating Systems For Aerospace and Its Support

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Research and development was required to lower the VOC of two component urethanes while avoiding problems created by high solids systems on aircraft. Without such research, there was very little hope to lower VOC content in this industrial segment.

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

A discussion of newer technologies for aerospace to reduce or remove VOC and hazardous air pollutants requires a short history as a prelude. Prior to 1988, most finish coats on aircraft and ground support equipment were coated with a two component urethane. Military equipment was coated with a specification, Mil-C-83286, which had a VOC of 600 g/l (5 lbs. per gal.) as a normal figure. Commercial aircraft operated under different specification, but the VOC was at a similar value. In 1988, the specification, Mil-C-85285B, was issued which required VOC maximums of 420 g/l (3.5 lbs. per gallon) for aircraft and 340 g/l (2.8 lbs. per gallons) for ground support. These coatings began their inroads into the military market in late 1988. The savings in VOC were significant and even more than some realized when the square foot coverage was considered.

The following shows the calculations for actual VOC reductions on a typical camouflage product.

Mil-C-83285, color 36375
32.3% solids volume
577 g/l (4.82 lbs.) VOC
618 sq. ft./gal. at 1 mil dry

Mil-C-85285B Type I, color 36375
52.3% solids volume
420 g/l (3.5 lbs.) VOC
840 sq. ft./ gal. at 1 mil dry

1000 gallons of Mil-C-83286 covers 518,000 sq. ft.
1000 gallons of Mil-C-83286 contains 4,820 lbs. of solvent
617 gallons of Mil-C-85285 Type I covers 518,000 sq. ft.
617 gallons of Mil-C-85285 Type I contains 2160 lbs. of solvent

Savings of 2660 lbs. of solvent

With these types of savings, great strides had been made and research continued to lower the VOC's, but the high solids had created some situations that meant higher solids may not be the most desirable resultant materials.

These main situations presented by the higher solids urethanes were:

1. Difficulty in controlling film thickness
   a. higher weight
   b. reduction in VOC savings
   c. outgassing

2. Shorter pot life

3. Higher viscosities giving rise to more orange peel, and exaggerated by newer high transfer efficiency guns.

4. Slow cure response at lower temperatures.

It was evident that higher and higher solids would only compound these problems. The logical approach was to use water to be able to lower application solids and still use high performance systems for aerospace systems. The use of exempt solvents such as 1,1,1 trichloroethane were not considered as a logical solution for long term research. Water was the only logical approach to lower VOC and still apply thin films.

The question became how low can we go? Two systems have been developed and tested to a proposal specification of Mil-C-83286 low VOC version. One material has a VOC of less than 250 g/l and its prototype have had limited applications on aircraft. The other material has approximately zero VOC, and is just in the final research phases with no large scale applications as of January 1995. The term "zero VOC' or approximately zero is based on theoretical calculations. The test methods involved in water determinations at this time have high enough percentage errors to yield fluctuating values. Some of these can even be negative values which would be wonderful, but not real.

The following graphs show how these results can vary. This is only presented to justify the use of theoretical VOC values in this presentation.

The following charts show the general characteristics and performance results to the proposed Mil-C-83286 low VOC draft specification. It must be noted that this is not a specification for use and has only been drafted as a guide to follow for development purposes, however, the majority of requirements exceed those of Mil-C-83286 and Mil-C-85285.

Specification	Two Component Urethane Water Based at 210 g/l VOC
Drying Time	
Set to Touch 2 hours	2 hours
Dry hard 8 hours	8 hours
Viscosity 15 to 30 seconds #4FC	25-30 seconds
Pot Life 4 hours minimum	4 hours
VOC 210 g/l max	210 g/l
Gloss Camouflage 85°/5 max	2
Gloss 20°/85 min	60° 85
Hiding Power .94 minimum	.98
Surface smooth and uniform	Uniform
Wet Tape 24 hours	No Effect
Impact Flexibility 20%	10% to 15%
Heat Resistance 4 hours @ 300°F	10% impact
Low Temperature Flexibility-2 inch mandrel	Passes 2 inch
Fluid Immersion	
Lube Oil Mil-L-23699 24 hours @ 150°F	H hardness
Hydrocarbon TT-S-735 Type III 14 days	F hardness
Hydraulic Fluid Mil-H-83282 14 days	H hardness
Hydraulic Fluid Mil-H-5606 14 days	H hardness
Skydrol 500B 14 days	F hardness
Distilled water 4 days @ 100°F	F hardness, Tr blisters
Jet Fuels 14 days	H hardness
Accelerated Weathering No Significant Changes	ΔE less than 1
Pencil Hardness (no requirement)	H

Specification	Two Component Urethane Water Based at Zero VOC
% Application Solids by Volume (no requirement)	39%
Drying Time	
Set to Touch 2 hours	2-3 hours
Dry hard 8 hours	10 hours
Viscosity 15 to 30 seconds #4FC	20 seconds
Pot Life 4 hours minimum	4 hours
VOC 210 g/l max	0
Gloss Camouflage 85°/5 max	3 @ 60° 3 @ 85°
Gloss 20°/85 min	88
Hiding Power .94 minimum	.98
Surface smooth and uniform	Smooth
Wet Tape 24 hours	No Effect
Impact Flexibility 20%	40%
Heat Resistance 4 hours @ 300°F	Passes 20%
Low Temperature Flexibility-2 inch mandrel	Passes 2 inch
Fluid Immersion	
Lube Oil Mil-L-23699 24 hours @ 150°F	H hardness
Hydrocarbon TT-S-735 Type III 14 days	H hardness
Hydraulic Fluid Mil-H-83282 14 days	2H hardness
Hydraulic Fluid Mil-H-5606 14 days	2H hardness
Skydrol 500B 14 days	F hardness, 30 days
Distilled water 4 days @ 100°F	3H hardness
Jet Fuels 14 days	2H hardness
Accelerated Weathering No Significant Changes	ΔE less than 1
Pencil Hardness (no requirement)	2H-3H
% Application Solids by Volume (no requirement)	50%

The information in the testing data shows these two separate two component urethane systems can perform to the majority of the desired requirements. Some fluctuation may occur as the products are commercialized and total field condition impacts are seen.

Areas of future work will concentrate on pot life and dry time controls at various humidities.

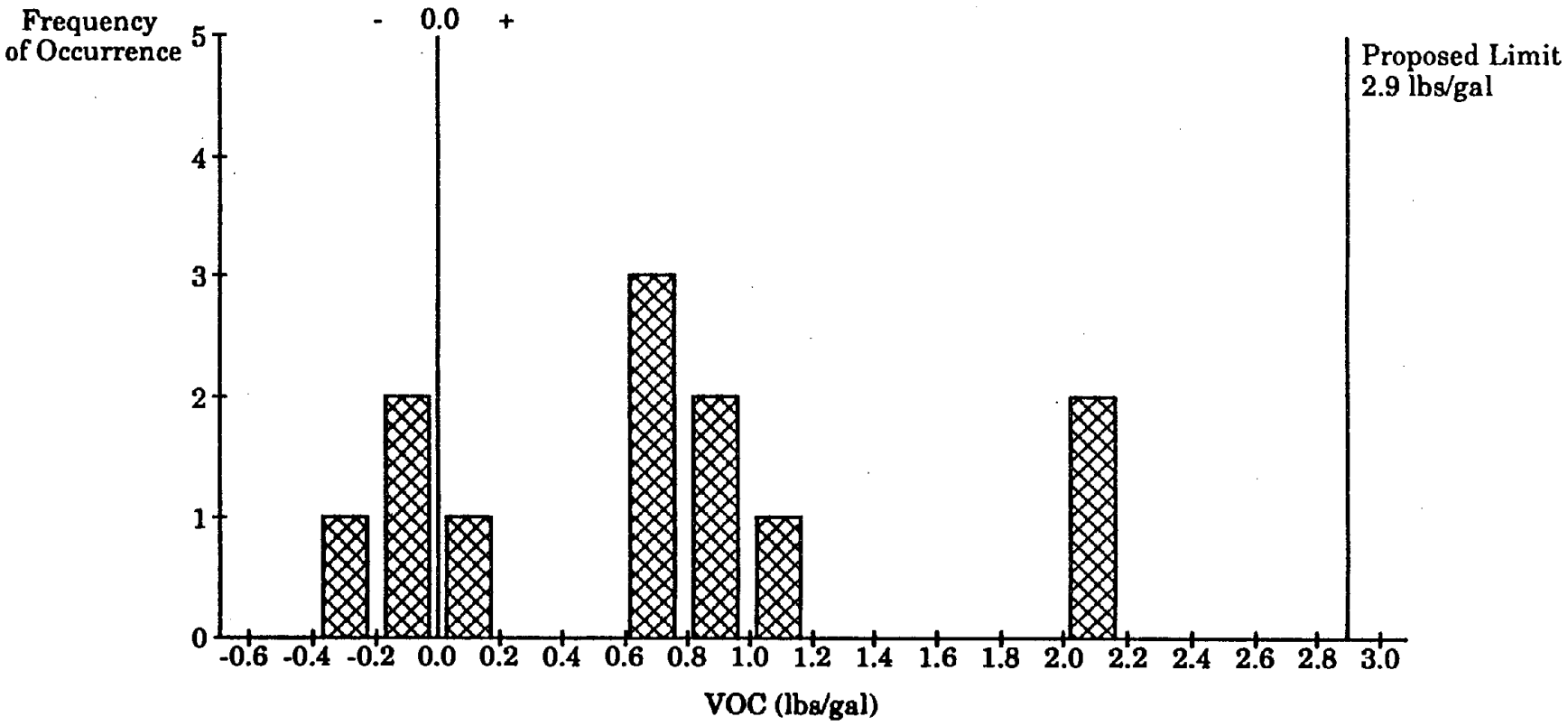

Figure 1 - Illustration of Method 24's lack of repeatability within a single laboratory for water-reducible primer. Note that some values are negative.

Source: Boeing Commercial Airplane Group

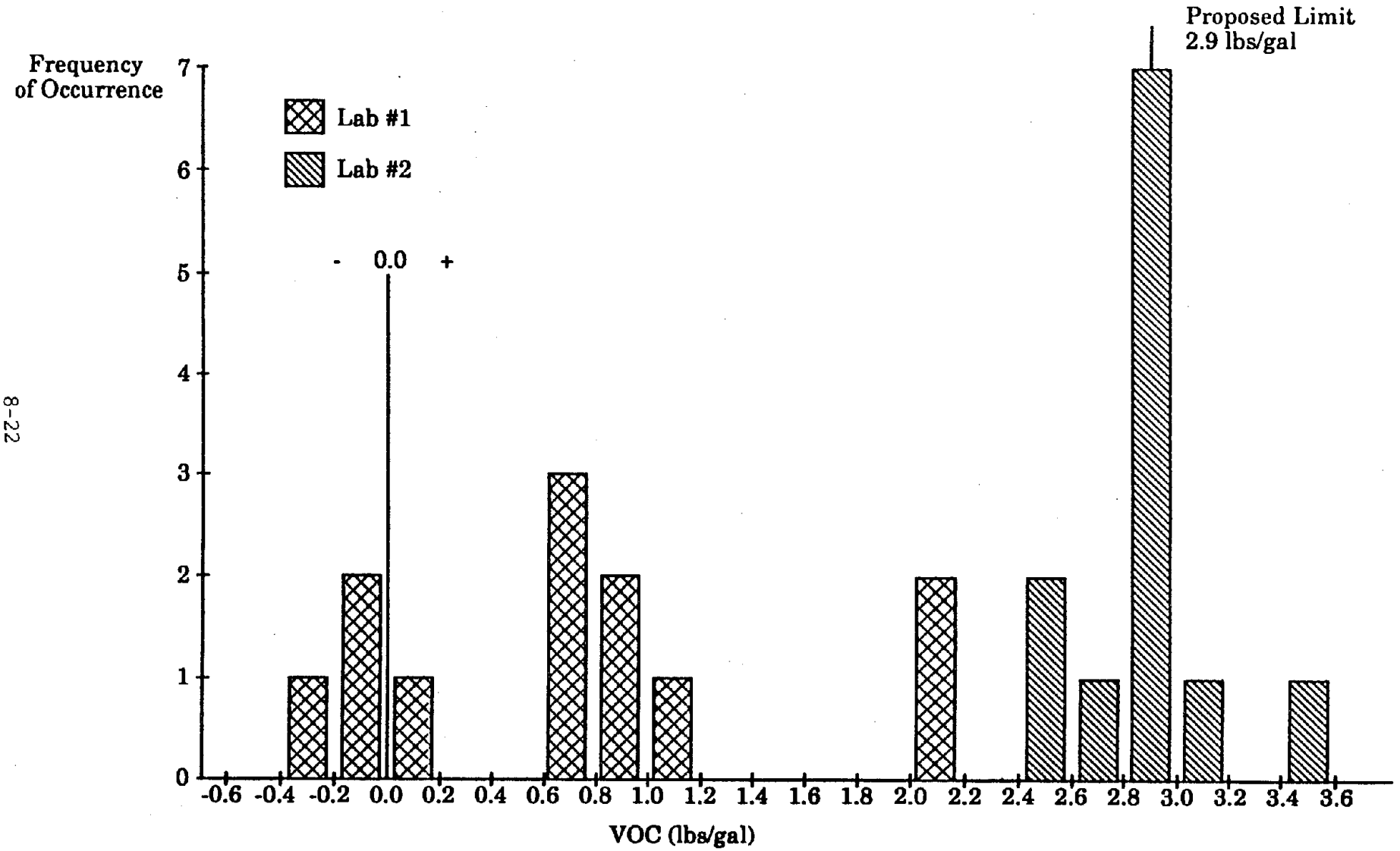

Figure 2 - Illustration of Method 24's lack of reproducibility between laboratories for water-reducible primer.

Source: Boeing Commercial Airplane Group

LOW VOC MARINE COATINGS

CHARLES F. AYRES

JOTUN/VALSPAR MARINE COATINGS

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

The marine environment contains many of the most corrosive atmospheric elements to be found anywhere on this planet. Ultra violet rays both direct and reflected from the surface of the water. Constant salt spray, high condensing humidities and even acid rain. These extreme conditions make the protection of metal a severe problem. Add to this intermittent immersion and total immersion in sea water for 24 - 36 months.

Fouling below the water by animal and plant organisms and extreme variations in climatic conditions round out this assault. Marine coatings are formulated to handle these varying degrees of assault.

Marine coatings are either applied in a shipyard where all necessary equipment is available to handle any situation, or applied by the crew of the ship where a roller and brush are the only tools available. Shipyards were able to apply so called 'exotic' coatings such as epoxies and urethanes. Full systems are shipyard applied from the primer to the topcoat. Ships crews on the other hand are mainly limited to maintenance and light repair work. The coatings are one pack and very user friendly. The basic coatings in this category were usually pure or modified alkyds. All of these coatings were historically high VOC because the technology or the need wasn't there to do anything differently.

California was the leader in reducing pollution. Rule 3 & Regulation 66 were the precursors of things yet to come. Louisiana was the next state to establish VOC regulations. Then came the Clean Air Act of 1990 which established the fact that the paint industry was part of the problem and we would have to reduce VOC's. The list of Hazardous Air Pollutants (HAP) was also out and many of the solvents used were on this list as well.

At this time many paint companies already had paints that met California rules and a separate line of coatings for the rest of the country. The California paints were harder to use and did not perform as well as the other paints. As stated before the technology was not always available. Raw material suppliers did not see the profitability in formulating products for one state.

What happened? With the Clean Air Act the industry had no choice but to change. A great deal of research has been done by raw material suppliers and paint manufacturers to develop low VOC products as good as or better than the high VOC coatings. Some technology has fallen by the wayside.

Lacquer dry coatings such as chlorinated rubber and vinyl may be a thing of the past. To get to the required VOC of 2.8 and still have a usable viscosity creates a challenge for the resin and coating formulator which is extremely difficult.

Alkyds have been developed to 2.8 #/gal. VOC. These products are generally higher in viscosity but are able to be applied with a brush, roller, or spray equipment. A little slower dry than the traditional alkyd coatings in most cases. As

with most of the low VOC coatings care must be taken to only get the required film build for proper dry.

Water base inorganic zinc primers have been around for quite a few years. Low VOC solvent based inorganic zinc primers have been developed. These can be used in the same applications as their predecessors.

Water borne coatings have come a long way also. Resins have been developed to give more durable coatings with good gloss retention. Single pack water borne acrylics can be formulated which are just as good as their solvent base counter parts. Early water resistance is being improved. Water borne epoxies have been developed that even have resistance to immersion. Basic drawback with using water is that it cannot be applied below 40°F.

Solvent borne and 100% solid epoxies. Resins have been developed with lower viscosities but equal performance to high VOC coatings. Generally these coatings either have no pot life or a very short pot life and must be used with plural component spray equipment.

Equipment has been developed to handle low VOC coatings that have high viscosities. Airless spray pumps have high ratios so that the paint is pumped at higher pressures. High Volume Low Pressure (HVLP) conventional equipment has been developed. It is good for spraying small areas with high viscosity coatings but is not fast enough for large areas such as ships hulls.

Two other areas of coatings are powder coatings and flame spray. Powder coatings in their present form are suitable for

small items that can be removed from the ship and painted in a shop. They require electrostatic application and curing at high temperatures. Flame spray can be done in situ. It is slow but very expensive.

The marine paint industry has met the challenge to make low VOC coatings that are able to protect marine structures. We are still making improvements in coatings and are always on the look out for new technologies to make better coatings that are environmentally friendly.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Evaluate Alternative Paint Stripping Technologies Used in Aircraft and Space Vehicles

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Abstract

Solvent strippers have been widely used to remove industrial coatings for many years. Normally used at room temperature, strippers can remove a wide range of organic coatings without attacking underlying metal substrates. Maintaining the integrity of metallic and nonmetallic substrates is a crucial requirement for the aerospace industry. The minimum acceptable control technology standard will target methylene chloride which is the main ingredient of the chemical paint strippers used presently. To meet the new regulations, an agreement to study alternative depainting techniques was signed by EPA and the National Aeronautics and Space Administration (NASA) in 1993. Other partners include the Air Force, commercial airlines, and aircraft manufacturers. A technical advisory committee was formed to recommend the testing protocol for the technologies to be evaluated. Seven non-hazardous air pollutant alternative stripping techniques have been identified and will be evaluated at NASA on either real aircraft panels or on accelerated aged panels. The alternative techniques are biodegradable or water-based chemical strippers, a carbon dioxide (CO_2) pulsed laser, the Flashjet system, high-pressure water stripping, plastic media blasting, sodium bicarbonate wet stripping, and wheat starch blasting. Elimination of methylene chloride can result in better technical performance, cost savings in materials and hazardous waste treatment, reduction of overall emissions, and fewer reporting requirements.

Evaluate Alternative Paint Stripping Technologies Used in Aircraft and Space Vehicles

Charged by Congress to protect the Nation's land, air, and water resources, the Environmental Protection Agency (EPA) strives to formulate and implement actions leading to a compatible balance between human activities and continuing viability of natural systems. To minimize continuing threats to public health and the environment from the use of paint removal products containing hazardous air pollutants, an interagency agreement to study alternative depainting technologies was signed between EPA and the National Aeronautics and Space Administration (NASA), Marshall Space Flight Center (MSFC). A similar agreement was also reached with the U.S. Air Force (USAF). Each agreement focuses on the evaluation and testing of depainting systems which do not use methylene chloride or any of its sister polluting agents.

Solvent strippers have been widely used to remove industrial coatings for many years. Normally used at room temperature, solvents can remove a wide range of organic coatings without attacking underlying metal substrates. Maintaining the integrity of metallic and nonmetallic substrates is a crucial requirement for industries which maintain coated metal structures (e. g., aircraft, defense materiel, shipbuilding, automotive, and home appliance).

Paint removal techniques fall within the following categories:

ABRASIVE	Using brute force to weaken and remove the coating solely through sanding or scouring action
IMPACT	Relying on particle impact to crack the coating for removal
CRYOGENIC	Using extreme cold to make the coating more friable and induce differential contraction, resulting in debonding
THERMAL	Using heat to oxidize, pyrolyze, and/or vaporize the coating through attack of its weaker constituents
MOLECULAR BONDING/ DISASSOCIATION	Using non-hazardous chemicals to weaken or break molecular bonds in protective coatings

The selection of techniques for study and evaluation is driven by such factors as the characteristics of the structures to be cleaned (e. g., size, substrate hardness, heat tolerance), paint/coating compositions, desired substrate texture after coating removal (e.g., rough, smooth), cleaning rates (i.e., throughput needed for production volume), facility space, compatibility with other existing systems, tolerance for any waste products produced, initial capital outlay, and operating costs. The processes which were the main focus of initial literature searches were primarily focused on aircraft/spacecraft needs, where relatively soft, thin aluminum substrates make up the bulk of the finished surfaces to be cleaned. All parties concurred that it was not the intent of either interim or final reports to recommend one product or process over another, but rather to evaluate each depainting system to whatever depth was practicable and present a factual account of the strengths and limitations of each. End users must make their own decisions concerning implementation.

Alternatives

Replacement of hazardous materials (rather than monitoring and controlling their release) is an avoidance activity. The team is investigating replacements for depainting methods which use methylene chloride. Several alternatives have been identified, which strip paint in various ways:

- *CO_2 pulsed laser* systems remove organic coatings via pyrolysis or vaporization.

  The advantages of the laser stripper are:
  - Reduces solid waste to a fine ash
  - Effective on composites
  - Precision control
  - Reliable and repeatable stripping
  - Minimal temperature increase

  The disadvantages are:
  - Large initial capital investment
  - High technical skills required
  - Air emissions must be treated

- *FLASHJET*™ systems are similar, but they use thermal energy produced by xenon flash lamps to

soften the coating and a low pressure CO_2 particle stream to sweep away the softened coating.

The advantages are:
- High degree of control
- Small volume of waste

The disadvantages are:
- Applicable only to large aircraft
- Requires offgas and particulate collection
- Potential for products of incomplete combustion

- *High-pressure water stripping* completely eliminates the need for hazardous materials by using the impact energy of a water spray at 10,000 psi (68,948 kPa) or higher.

The advantages are:
- High stripping rate
- Water can be recycled
- Compatible with most treatment systems
- Automated fairly easily

The disadvantages are:
- Ultrahigh pressures require automation
- Improper operation can damage substrate
- Water can damage joints and seals

- Plastic media blasting chips away paint by optimizing blast particle hardness, geometry, and impact energy, eliminating paint flakes in a wastewater stream.

The advantages are:
- Produces no volatile organic compounds
- Has a high stripping rate
- Eliminates water usage
- Can selectively remove individual layers
- Recyclable
- No size limitations
- Fully developed systems available

The disadvantages are:
- Disposal of spent media
- Contaminants may damage substrate
- Media may close cracks
- Media are flammable
- Produces airborne particulate

- *Sodium bicarbonate wet stripping* sprays baking soda (an environmentally benign substance) suspended in water at medium to low pressures.

The advantages are:
- Process can selectively remove layers
- Inexpensive stripping media
- Liquid waste easily treated
- Water dissipates heat on substrate

The disadvantages are:
- Nonrecyclable
- Wet sludge may be hazardous waste
- Potential substrate damage

- *Wheat starch blasting* uses a controlled hardness of wheat starch applied via low-pressure air, which eliminates the handling of wastewater.

The advantages are:
- Media are nontoxic and biodegradable
- Inexpensive media
- Eliminates water usage
- Can remove layers selectively
- Safe for clad aluminum and composites
- Reusable media
- Media become more effective after use
- No volatile organic compounds generated

The disadvantages are:
- Low stripping rates
- Media can collect in cracks
- Media are moisture sensitive
- Contaminated media could be harmful
- Particles in media could damage substrate

- *Chemical stripping* products are available which are water-based and/or biodegradable, which means that they can be recycled and disposed of with minimal waste handling. Evaluations were conducted

on 31 products, focusing on spray-on, rinse-off chemicals at various dwell times.

Test Products for Chemical Stripping

Product	Vendor
3M Safest Stripper	3M Corporation
Heavy Duty Paint Stripper #539	AMAX Industrial Products Group
ARCOSOLV PM ACETATE and DPM ACETATE	ARCO Chemical Company
NMP and NMP-T	BASF Corporation, Chemical Division
Wright Way Stripper	BIX Processing Systems
Safety Strip 4000	Brulin Corporation
Back to Nature AP40, AP4l, VI, VII, and VIII	Dynacraft Industries
Dynasolve 711 and 750	Dynaloy, Inc.
Prep Rite	Ecolink, Inc.
EZE 540 and 542	EZE Products
F.O.2115A	Fine Organics Corporation
Ship Shape	International Specialty Products
Cee-Bee Stripper EI004B, El 092A, and E2000	McGean-Rohco, Inc.
Ultra Safe Stripper	National Solvent Corporation
Orchem LPI779BC	Orchem, Inc.
Parks Pro Stripper II	Parks Corporation
EG 566	PYROCK Chemical
Strypeeze Green Label Remover	Savogran Company
Turco 6776 and 6813	Turco Products
PSL-230	U S. Polychem Corporation

The advantages are:

- Strippers are nontoxic
- Safe for clad aluminum and composites
- No volatile organic compounds generated
- Ambient temperature process
- Low initial capital investment

The disadvantages are:

- Slow stripping rates
- Waste could be hazardous
- Nonrecyclable
- Labor intensive

Elimination of depainting materials and processes based on methylene chloride can result in better technical performance, cost savings in materials and hazardous waste treatment, reduction of overall emissions, and fewer reporting requirements.

SESSION 8B

ARCHITECTURAL AND INDUSTRIAL MAINTENANCE COATINGS

PAPERS PRESENTED:

"Evaluation of Innovative Low-Volatile Organic Compound Industrial Maintenance Coatings"
by
Dean Cornstubble
Research Triangle Institute
Research Triangle Park, North Carolina

"Solventless and Low-VOC Architectural Coatings Formulated from Novel Latexes with Low MFT and High T_g"
by
Thomas Schuman
University of Southern Mississippi
Hattiesburg, Mississippi

"Evaluation of Emissions from Latex Paint"
by
Bruce Tichenor
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, North Carolina

"New Polyurethane Prepolymers for Ultra-low VOC Plural Component Coatings"
by
Thomas Santosusso
Air Products & Chemicals, Inc.
Allentown, Pennsylvania

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Evaluation of Innovative Low-Volatile Organic Compound Industrial Maintenance Coatings

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INTRODUCTION

End users of industrial maintenance coatings in today's marketplace are becoming more critical of the coatings they select. Coatings must meet not only their performance expectations but also implemented State and, most recently, proposed Federal regulations for volatile organic compounds (VOCs). Users are concerned whether innovative coating technologies that are designed to meet VOC regulations will retain the quality and longevity performance characteristics of current, noncompliant coatings that are well respected in the field. Thus, end users, particularly small businesses, are looking for information from independent research studies such as this one that test and evaluate new industrial maintenance coating technologies.

To address these concerns, this research project identified and evaluated emerging low-VOC industrial maintenance coating technologies as pollution prevention alternatives to high-VOC solvent-borne coatings. In addition, this project provides end users with an independent evaluation of some new low-VOC coatings. Industrial maintenance coatings are defined as heavy-duty coatings, including primers, sealers, undercoats, and intermediate and top coats that are formulated to protect metal substrates from degradation when exposed to aggressive environments. Metal substrates include bridges, military equipment, ships, septic tanks, and all exterior steel structures. Aggressive environments to which these protected substrates are exposed include coastal, industrial, commercial, and institutional sites. Exposure includes frequent scrubbing or abrading, immersion in water or wastewater, and exposure to steam.

This paper presents the results of an evaluation of five industrial maintenance coating system alternatives compared to a standard high-VOC coating. Procedures used in this research study included determining each coating's physical properties, having three operators apply each coating system to a set of test panels consisting of two different substrates, and conducting four durability tests and a 3-month outdoor exposure test on the coated test panels. The results of this evaluation are intended to promote the use of low-VOC coatings in the marketplace, thereby reducing VOC emissions.

BACKGROUND

Research Triangle Institute (RTI), in collaboration with the U.S. Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory (AEERL), contacted coating formulators, resin manufacturers, industrial users, and trade organizations to help identify and target research needs and opportunities within a specific category of the architectural and industrial maintenance (AIM) coatings industry. The emphasis in these contacts was to identify low hazardous air pollutant (HAP) and low-VOC coatings. Representatives from AIM coating manufacturers, resin manufacturers, users, representative associations, and other associations affected by AIM coating regulations were contacted. The majority of these contacts were AIM regulatory negotiation committee members. Industrial maintenance coatings were identified as the highest priority for evaluating new low-VOC coatings.

A survey conducted by SRI International in 1990 for the National Paint and Coatings Association (NPCA) indicated that approximately 90.8 million liters (24 million gallons) of industrial maintenance coatings were sold in the United States in that year.[1] VOC content ranges for these coatings were 351 to 500 g/ℓ (2.9 to 4.2 lb/gal), with an average of 425 g/ℓ (3.5 lb/gal). Based on this average, the estimated national VOC emissions in the year 1990 were 38,590 Mg (42,538 tons). For every 50-g/ℓ (0.4-lb/gal) reduction in VOC content, the estimated national VOC emissions from manufacturers converting to low-VOC coating formulations would be reduced by 4,540 Mg (5,004 tons). Thus, this project was initiated to evaluate the technical feasibility of innovative low-VOC industrial maintenance coatings.

EXPERIMENTAL METHODS

Evaluation testing was designed on the basis of six discrete areas: coating systems, substrates, physical property testing, VOC emissions determination, and performance and outdoor exposure testing. Each section is discussed below.

Coating Systems

Coating systems evaluated are described generically in Table 1.

Table 1. Coating Systems Tested

Coating system	System coatings	Generic description
1	primer	solvent-borne, moisture-cured polyurethane
	intermediate	solvent-borne, zinc-rich, moisture-cured polyurethane
	topcoat	solvent-borne polyurethane
2	primer	waterborne epoxy ester
	topcoat	waterborne latex
3	primer	solvent-borne alkyd resin
	topcoat	waterborne acrylic
4	topcoat	solvent-borne, two-component polysiloxane epoxy
5	primer	water-reducible alkyd
	topcoat	waterborne acrylic
6 (standard)	primer	solvent-borne alkyd resin
	topcoat	solvent-borne alkyd enamel

Selection of these coatings was based on communications with coating suppliers who had new low-VOC products that were either just entering the market or had been on the market less than one year. The standard was randomly selected based on its high VOC content with respect to the EPA-proposed regulation and its applicability to most industrial maintenance settings.

Substrates

The use of test panels is common practice for evaluating paints and related coatings (see American Society for Testing and Materials [ASTM] Standard D 609 and ASTM Standard D 2201).[2] The most widely used substrates in industrial maintenance applications are ASTM A36 and ASTM A588 steels. ASTM A36 steel is an all-purpose carbon-grade steel used in building and bridge construction. ASTM A588 steel is a corrosion-resistant, high-strength, low-alloy steel that is suitable for use in the bare or uncoated condition where exposure to a normal atmosphere causes a tightly adherent oxide to form on the surface of the substrate protecting it from further oxidation. The A588 steel, when used as a coated substrate, is claimed to provide a longer coating life than other structural steels, such as A36.

A total of 216 test panels were ordered from the Jay Allen Steel Company in Pittsburgh, Pennsylvania: 108 of the A36 panels and 108 of the A588 panels. The dimensions of each test panel were 152.4 mm x 304.8 mm x 6.35 mm (thickness) (6 in x 12 in x 1/4 in). In the design of the experiment, six panels were assigned per substrate per coating system, with four of the panels sent to KTA-Tator in Pittsburgh, Pennsylvania, for durability testing and two sent to the LaQue Center in Kure Beach, North Carolina, for outdoor exposure testing.

Surface Preparation of Substrates

Surface contaminants that could reduce adhesion, such as grease, oil, dirt, or mill scale, were removed prior to painting. Upon arrival at the painting contractor's facility, each test panel was inspected by an operator. Inspection revealed little or no mill scale on each panel surface but did reveal the presence of grease and dirt. Mechanical cleaning was not necessary. For cleaning, operators cleaned each panel with rags soaked with lacquer thinner to remove surface contaminants.

Six panels of each substrate were then attached to a 1.2 m x 0.9 m x 0.013 m (4 ft x 3 ft x ½ in) wooden board by Velcro hook and loop strips. Each test panel was labeled with an identification number for data quality control. This configuration provided a total panel surface area of 0.54 m^2, 0.9 m x 0.6 m (6 ft^2, 3 ft x 2 ft) for each operator to apply each coating, giving an adequate amount of coating coverage for calculating each coating system's VOC emissions as applied.

Physical Properties of Each Coating

Before application, an operator thoroughly mixed each container of coating, then poured 7.6 to 11.4 ℓ (2 to 3 gal) of the coating into a standard 18.9 ℓ (5 gal) container. Three grab samples were taken from the center of the container. Each 500-mℓ (17-fl.oz) sample was delivered to RTI's analytical laboratory and analyzed, in triplicate, to determine the percent VOC content by volume percent water content (if the coating was waterborne), density, percent volume solids, and percent weight solids of each coating. The analysis method used was EPA Reference Method 24.[3] Volume solids and weight solids of each coating were derived from ASTM Standard D 2369.[2]

VOC Emissions Determination

VOC emissions, as applied, per operator per coating were determined from weight loss data of the standard 5-gal paint container and each coating's percent solids, by weight. Weight loss was determined by weighing the standard 5-gal container before and after each coating application using a Sartorius F32000S floor scale, with a capacity of 32 kg (71 lb) and a readability of 0.1 g (0.0002 lb).

Prior to coating application, each test panel, with Velcro strips and label attached, was weighed. The technique used to determine the weight of each test panel was to place a standard clean and empty 5-gal container on the center of the pan of the floor scale used to determine coating usage during application. The weight of the container was tared out. A test panel was then placed on top of the container in a centered position. Each test panel from each set of 12 panels (each set equals 12 test panels on each support board for each operator) was placed on top of the container in the same position. After weighing, the container was removed, the scale re-zeroed, and the container placed back on top of the scale for the next set of readings.

After the coating application phase of the test was complete, test panels were removed from their wooden supports and laid horizontally side by side on plywood panels away from the test area. They were allowed to air-cure in this position for a minimum of 7 days. After air curing, each test panel was reweighed to determine the amount of coating solids remaining on each panel. The same floor scale was used to determine these weights.

Performance Testing

Four test panels from each coating, substrate, and operator combination were shipped to KTA-Tator in Pittsburgh, Pennsylvania, for durability testing. Each test panel was subjected to four performance tests: impact resistance (ASTM D 2794); adhesion (ASTM D 3359); methyl ethyl ketone (MEK) rub (ASTM D 4752); and pencil hardness (ASTM D 3363).[2] A test matrix representing the number and type of panels per coating system tested was designed: three panels per test per substrate (for three operators each) per coating system for each test panel, resulting in a total number of 72 panels tested for five coating systems and the standard.

Outdoor Exposure Testing

The LaQue Center in Wrightsville Beach, North Carolina, conducted a 3-month exposure test of the remaining 72 panels. This test site is one of four outdoor exposure testing facilities in the United States. The test site is classified as a severe marine atmospheric environment.

LaQue Center personnel arranged each test panel on exposure racks in a testing area, 25 m (82 ft) from the Atlantic Ocean, at their Kure Beach, North Carolina, facility. In addition, they performed and documented, as necessary, the following tests: dry film thickness (DFT) of the coating on each pane; gloss measurements of each panel prior to exposure on the racks per ASTM Standard D 523; scribed each panel per ASTM Standard D 1654; exposed each panel at 30° to the horizontal facing the Atlantic Ocean for 3 months; and photographed all coated panels together.

After exposure, each panel was inspected for: gloss, before and after washing, per ASTM Standard D 523; chalking per ASTM Standard D 4214 (Test Method C); blisters per ASTM Standard D 714; creepage at the scribe per ASTM Standard D 1654; and rust per ASTM Standard D 610. A photograph was taken of each panel while on the exposure racks; a group photo of each set of six panels (per substrate per coating system) and one photograph of the most severely affected panel in the set were taken.

RESULTS

The results from this evaluation include analyses of each coating's physical properties, calculations of VOC emissions as applied, and results from performance and outdoor exposure testing. Performance and outdoor exposure results were used to provide end users with a qualitative assessment of each coating's applicability to field service. The following sections describe each evaluation and its results.

Coating Analysis

The underlying purpose for analyzing each coating was to determine VOC content, density, solids weight percent, and water content in weight percent. VOC content values were used to provide a comparison against the proposed EPA VOC content limits for the years 1996 and 2000 and for the year 2004. Density and solids weight percent were used to calculate VOC emissions. Water content in weight percent was analyzed to show the amount of water in each waterborne coating. Table 2 summarizes the analytical results.

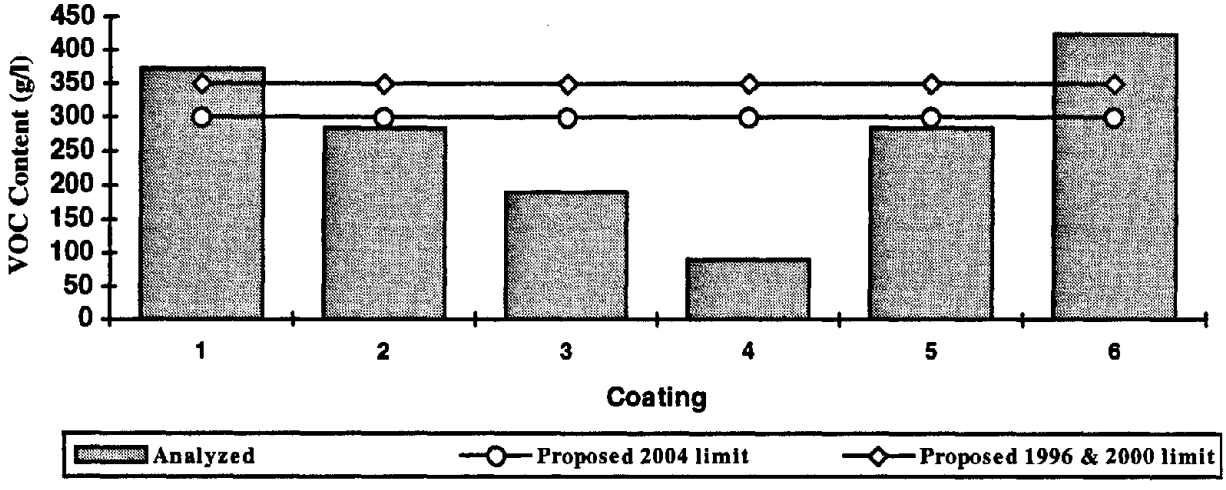
Table 2. Results of Coating Analyses [a]

Coating system	Sample	VOC content [b,c,d] (g/ℓ)	Density (g/cm^3) [e]	Solids content (wt. %)	Water content (wt. %)
1	primer	360	2.4	85	- [f]
	intermediate	360	1.6	78	-
	topcoat	372	1.3	71	-
2	primer	283	1.2	44	46
	topcoat	284	1.2	49	38
3	primer	394	1.4	72	-
	topcoat	190	1.1	45	47
4	topcoat	84(mixed) [g]	1.3 [g]	NA [h]	NA
5	primer	237	1.2	37	56
	topcoat	284	1.2	40	49
6 (standard)	primer	394	1.4	72	-
	topcoat	424	1.0	57	-

[a] Values shown are the mean of six samples per coating.
[b] VOC content as applied, minus water, of each sample analyzed.
[c] 1 g/ℓ = 0.008345 lb/gal.
[d] No bias was determined for VOC content measurements although they tended to run 3 to 7 percent higher than values provided by the manufacturers.
[e] 1 g/cm^3 = 62.43 lb/ft^3.
[f] No water detected.
[g] Manufacturer's numbers were used.
[h] NA = Not available since EPA Method 24 could not be used.

VOC Content

Figure 1 compares analyzed VOC content versus the EPA-proposed VOC content limits for the years 1996 and 2000 and for the year 2004. Of the six coating systems evaluated, systems 2, 3, 4, and 5 met the EPA-proposed VOC content limits. Coating system 4, which was the two-component polysiloxane, could not be analyzed by the testing laboratory using EPA Method 24. The manufacturer's value for VOC content was used.



[NOTE: 1 g/ℓ = 0.008345 lb/gal]

Figure 1. Average VOC Content for Each Coating System

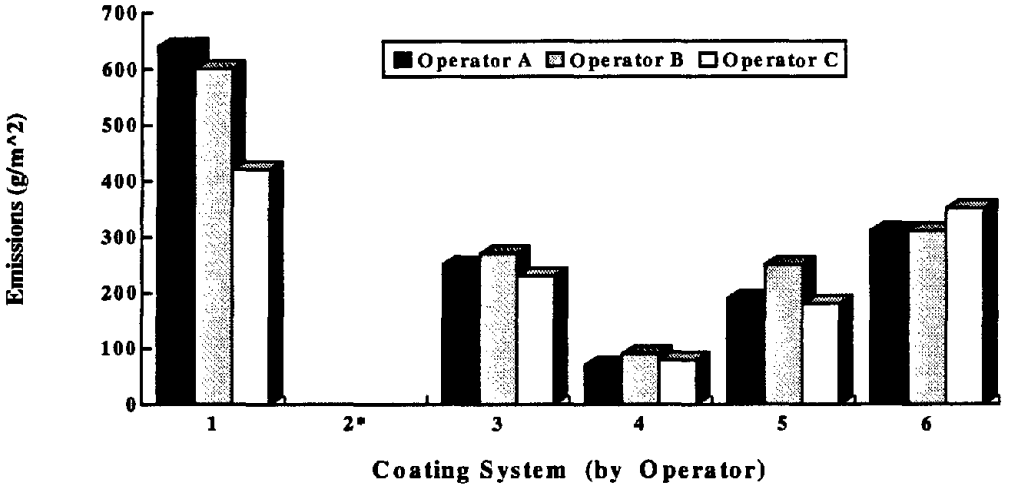
VOC Emissions

Figure 2 shows that the average VOC emissions of coating systems 3, 4, and 5 were lower than those of system 6 (the standard). Over time, the lowest-VOC content coating system would prove to be a better system than the standard with respect to VOC emissions if the durability (*i.e.*, service life) and cost of that system were equivalent.

Performance Testing

Table 3 ranks each coating system by performance test. The purpose of this ranking is to provide a representative idea of how each coating system performed overall and how each system compared to the standard with respect to performance testing. Each test was assigned a point value on a scale of 1 to 5, each unit depending on the scale for each test. This rating system was selected because each of the test results could be conveniently divided into five sections. Refer to each test separately described below for definitions related to each test's rating definition.

All coating systems outperformed the standard. Coating system 4 outperformed all other coatings and was shown to be the best performing in durability. The following sections describe the results of each performance test as they related to the ASTM standard test methods employed.



* Weight data for coating system 2 not available. [NOTE: 1 g/m^2 = 0.295 lb/in^2]

Figure 2. VOC Emissions as Applied per Unit Area

Table 3. Ranking of Each Coating System
(Performance Testing)

Sub-strate	Coating system	Impact resistance	Adhesion		MEK resistance		Hardness		Total	*Rank*
			Method A	Method B	To primer	To metal	Scratch	Gouge		
A36	**1**	3	5	-	5	5	5	3	26	***2***
	2	5	-	4	1	5	3	3	21	***3***
	3	3	-	3	2	5	2	2	17	***6***
	4	5	5	-	5	5	5	4	29	***1***
	5	5	-	5	1	2	5	2	20	***4***
	6 (standard)	2	-	1	5	5	3	2	18	***5***
A588	**1**	4	5	-	5	5	4	3	26	***2***
	2	5	-	5	1	5	3	3	22	***3***
	3	4	-	3	2	5	5	2	21	***4***
	4	5	-	5	5	5	5	3	28	***1***
	5	5	-	5	1	2	5	2	20	***6***
	6 (standard)	3	-	2	5	5	4	2	21	***4***

(continued)

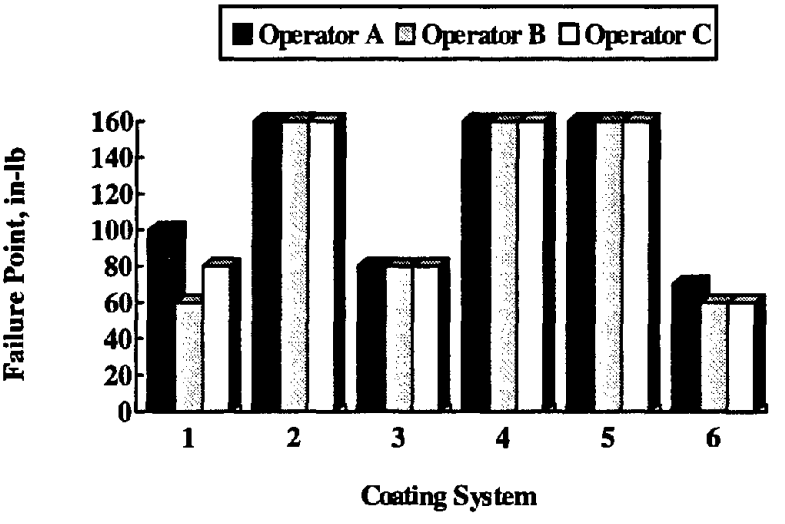
Table 3. Ranking of Each Coating System (continued)

Rating Definitions (mean of three operators):

Rating	Impact resistance	Adhesion	MEK resistance (Double rubs to surface)	Hardness
1	0-30	0-1	1-10	1-3
2	31-60	2	11-20	4-7
3	61-90	3	21-30	8-11
4	91-120	4	31-40	12-13
5	121 +	5	41 +	14

Impact Resistance: ASTM Standard D 2794. According to ASTM, the impact resistance test method has been found to be useful over many years in predicting the performance of organic coatings for their ability to resist cracking caused by impacts. This test measures the indentation that results when a painted panel is struck with a hard object such as a steel ball. Results of impact testing are illustrated in Figure 3 for A36 and A588 substrates. Clearly, coating systems 2, 4, and 5 performed best, having an end failure point of 8.96 m-kg (160 in-lb). The standard, along with systems 1 and 3, showed poor performance in comparison to systems 2, 4, and 5. Their end failure point was 5.60 m-kg (100 in-lb) or less. All coating systems proved to be equal to or better than the standard's 3.36 m-kg (60 in-lb). Results are also summarized in Table 3.

Adhesion: ASTM Standard D 3359. Because the substrate and degree of surface preparation have a drastic effect on coating adhesion, this method of evaluating a coating's adhesion to different substrates or surface treatments, or of different coatings to the same substrate and treatment, is of considerable usefulness



[NOTE: 1 in-lb = 0.056 m-kg]

Figure 3. Impact Resistance (Average of Substrates A36 and A588)

to the coatings industry. In this test, a strip of tape is used to measure the amount of coating removal from a scribed 'X' on the painted surface. As shown in Table 3, coating systems 1, 2, 4, and 5 performed the best, with adhesion ratings of 4 and 5. System 3 and the standard showed poor performance with adhesion ratings of 3 and 2. For systems 1 and 4, both adhesion methods (A and B) were used because of differences in DFTs on each of their panels. For system 1, the DFT on each test panel was an average of 0.030 cm (11 mils [0.011 in]), whereas for coating system 4, some panels measured more than 0.013 cm (5 mils [0.005 in]) DFT. This variation was due primarily to operator skill level and, in the case of coating system 4, mishandling of several panels during application, which resulted in reapplied coating. For all coating systems, adhesion performance on A588 substrates was consistently better than on A36 substrates. This showed that adhesion between the coating system and the substrate was markedly improved by the thin oxide layer on the A588 panels.

MEK Rub: ASTM Standard D 4752. The MEK rub test method is used primarily for assessing the MEK resistance of ethyl silicate (inorganic) zinc-rich primers. However, this test method was chosen as a good indication of how each coating system would stand up to a strong and commonly used chemical solvent such as MEK. In this test, an MEK-saturated cloth was continually rubbed over each coated panel until either the metal substrate was exposed or 50 double rubs was reached. A double rub is defined as a back-and-forth motion of approximately 2 in (50 mm) in length over a specified test area on the panel. For this test, double rubbing was evaluated on both the topcoat and the primer (by scraping away topcoat). Table 3 shows that MEK performance was consistently superior for coating systems 1, 4, and the standard. The results for coating systems 2 and 3 showed poor performance of their topcoats on both substrates, whereas their primers showed excellent performance on both substrates. Coating system 5 showed poor performance in all cases. Coating systems 1 and 4 had equivalent results. Both coating systems showed high tolerance for the MEK rub test.

Pencil Hardness: ASTM Standard D 3363. Film hardness of a coating can be rapidly and inexpensively determined by drawing pencil leads of known hardness across a test area. The procedure called for a technician to draw pencils of decreasing hardness across a specified test area until a pencil was found that would neither cut through nor scratch the surface of the film. Any defacement of the film other than a cut (gouge) was considered a scratch.

Interpretation of the data from this test is best illustrated in Table 4. The resulting pencil hardness of each coating system by substrate and by each endpoint test (either scratch or gouge) was assigned a number for clarity of data presentation. For example, a pencil hardness of 6B was equated to a 1, a pencil hardness of 5B was equated to a 2, and so on up to 6H which was equated to a 14. Based on these numerical assignments, a generic rating of excellent, very good, good, fair, and poor was given to each test for each substrate and coating system.

Tables 3 and 4 show that coating systems 1, 4, and 5 had the greatest hardness resistance of 12 to 14 (4H to 6H) on both substrates in the scratch test, but proved to be fair to good, 4 to 11 (3B to 3H), in the gouge tests. Coating system 2 showed a hardness range of 8 to 11 (H to 2H) on both substrates. System 3 proved to perform best only on the A588 substrate in the scratch test. The standard, coating system 6, showed moderate performance in both tests on both substrates. Coating system 4, however, outperformed all other coating systems in the pencil hardness tests with an 8 to 14 rating (F to 6H pencil hardness).

Outdoor Exposure Testing

Outdoor exposure testing of each coating system was evaluated at the LaQue Center's marine atmospheric testing area located 25 m from the Atlantic Ocean. The exposure date was August 18, 1994,

Table 4. Pencil Hardness Rating for Each Coating System

	Coating system					
Test result	**1**	**2**	**3**	**4**	**5**	**6**
A36-Scratch	E	G	F	E	E	G
A588-Scratch	VG	G	E	E	E	VG
A36-Gouge	G	G	F	VG	F	F
A588-Gouge	G	G	F	G	F	F

E = Excellent (14); VG = Very Good (12-13); G = Good (8-11); F = Fair (4-7); P = Poor (1-3). Values in parentheses are mean values of operators A, B, and C.

and the inspection date was December 1, 1994, for a total exposure period of 15 weeks. Orientation of the exposed panels was 30° facing the ocean (east). Table 5 ranks each coating system by exposure test. Each test was assigned a point value on a scale of 0 to 10.

Table 5. Ranking of Each Coating System [a]
(Outdoor Exposure Testing)

Sub-strate	Coating system	Gloss	Creepage	Rust	Blisters	Chalk	Total	*Rank*
A36	**1**	8	10	10	10	10	48	***1***
	2	0	7	10	10	10	37	***6***
	3	5	7	10	10	10	42	***3***
	4	10	4	10	10	10	44	***2***
	5	8	6	8	10	10	42	***3***
	6 (standard)	6	7	10	10	8	41	***5***
A588	**1**	8	10	10	10	10	48	***1***
	2	0	7	10	10	10	37	***6***
	3	5	8	10	10	10	43	***3***
	4	10	4	10	10	10	44	***2***
	5	8	7	7	10	10	42	***4***
	6 (standard)	6	8	10	10	8	42	***4***

[a] Mean of three operators.

Only coating systems 1, 3, and 4 outperformed the standard. Coating system 1 outperformed all other coatings and was shown to be the best performing in weathering durability. The following sections describe each test performed on each panel at the conclusion of exposure testing.

Creepage: ASTM Standard D 1654. A 5-cm (2-in) scribe was made on the lower half of each test panel according to the procedures in ASTM Standard D 1654 prior to exposure. The representative mean, maximum, and minimum of creepage, corrosion, or loss of paint extending from the scribe mark, was recorded.

As illustrated in Table 5, coating systems 2, 3, 5, and 6 showed creepage between 0.5 and 3.0 mm (1/64 to 1/8 in) over the 3-month exposure period. Coating system 4 performed the worst with creepage between 3.0 and 7.0 mm (1/8 to 1/4 in). Interestingly, coating system 1 outperformed all other systems with zero creepage from the scribe. This could be due to the larger film thickness of a three-coating system versus the smaller film thicknesses of the other coating systems. In comparison to the standard, only coating system 1 showed superiority in paint retention at the scribe over the other coating systems.

Rust: ASTM Standard D 610. The degree of rusting on each test panel was determined by the percent of the area rusted. These percentages were converted into a rust grade scale ranging from 0 to 10 as shown in Table 5. Only coating system 5 showed significant rusting. All other systems, including the standard, showed very little rusting.

Blistering: ASTM Standard D 714. The degree of blistering of each test panel, according to ASTM Standard D 714, was evaluated by comparing each exposed surface to a photographic reference standard. Reference standards were selected by ASTM in four steps corresponding to size on a numerical scale from 10 to 0, in which No. 10 represents no blistering. Blistering standard No. 8 represents the smallest size blister easily seen by the unaided eye. However, as illustrated in Table 5, no blistering occurred (10) on any of the six coating systems evaluated for either substrate.

Chalking: ASTM Standard D 4214 (Test Method C). By definition, chalking is the formation on a pigmented coating of a friable powder evolved from the paint film itself at, or just beneath, the surface. Method C was used for evaluating the degree of chalking on each test panel. Table 5 shows the results of chalking on substrates A36 and A588 by coating system and by operator. A 10 indicates no film formation on the surface of the test panel. An 8 indicates a slight film formation. As shown, coating systems 1 through 5 outperformed system 6 with a 10 rating as compared to an 8 rating. No distinction can be made between each of coating systems 1 through 5.

Gloss: ASTM Standard D 523. Gloss measurements were taken with a Minolta Multi, Gloss 268, at a 60° orientation. Gloss measurements of each test panel were taken at three separate intervals: after the initial setup, before washing with water and a mild detergent solution, and after washing.

Table 6 reveals the same pattern for either substrate where the initial gloss for coating systems 1, 4, and 6 were consistently higher than for systems 2, 3, and 5. With respect to gloss retention from initial setup to post-washing of the panels, coating systems 4 and 5 were the best, having relatively the same gloss for both substrates. However, coating system 2 was the only coating system to have an increase in gloss from initial setup to post-washing for both substrates. This was possibly due to additional curing and/or loss of VOCs or to the sloughing off during exposure of pigmentation within the paint system, which is typically added to achieve gloss specifications. Gloss for coating systems 3 and 6 decreased the most out of all systems. In comparison to the standard, coating systems 1 and 4 had the highest degree of gloss and the most gloss retention after exposure.

Table 6. Gloss Reduction

	Coating system	Initial gloss	Final gloss	Percent reduction
A36	**1**	86	71	17
	2	40	56	-40
	3	25	12	52
	4	85	82	4
	5	54	46	15
	6 (standard)	75	42	44
A588	**1**	85	70	18
	2	33	45	-36
	3	23	11	52
	4	74	70	5
	5	29	24	17
	6 (standard)	66	38	42

SUMMARY

Table 7 summarizes ranking results of each coating system evaluated for VOC emissions and durability and outdoor exposure testing. For both substrates A36 and A588, coating system 4 performed the best while outperforming the standard. Coating system 1 performed well but had high VOC emissions.

Table 7. Summary of Overall Coating System Performance

Sub-strate	Coating system	Ranking			Sum of ranks[a]	*Overall rank*
		Emissions	Durability	Outdoor exposure		
A36	**1**	5	2	1	8	***2***
	2	NA[b]	3	6	?	***?***
	3	3	6	3	12	***4***
	4	1	1	2	4	***1***
	5	2	4	3	9	***3***
	6 (standard)	4	5	5	14	***5***
A588	**1**	5	2	1	8	***2***
	2	NA	3	6	?	***?***
	3	3	4	3	10	***3***
	4	1	1	2	4	***1***
	5	2	6	4	12	***4***
	6 (standard)	4	4	4	12	***4***

[a] Emissions, durability, and outdoor exposure ranks were summed to give overall ranking.
[b] Not available

CONCLUSIONS

The objective of the evaluation was to compare VOC emissions, as applied, of alternative low-VOC industrial maintenance coating systems to a standard. The results of performance testing in conjunction with the 3-month outdoor exposure test were inconclusive as to a coating system's service life. However, some conclusions can be made from this evaluation as to the degree of VOC emissions reduction of the coating systems tested versus the standard.

- The tables and figures presented in this paper show that VOC emissions were dependent on several factors, including the VOC content of each coating layer of each coating system, the number of coating layers per system, and the amount of coating applied (as recommended by the manufacturer). However, these tests have shown that the solvent-borne, two-component polysiloxane epoxy and the multi-layer, solvent-borne polyurethane coating systems were better than the standard, a solvent-borne alkyd.

- The solvent-borne, two-component polysiloxane epoxy coating system achieved excellent ratings in most categories of testing and was the lowest VOC content coating (by a factor of 4 versus the standard).

- Although the multi-layer, solvent-borne polyurethane coating system had higher VOC emissions than the standard, it is apparent from the emissions data that number of coatings and film thickness played a major role in producing such high emissions. Thus, a low VOC content for a coating does not necessarily mean lower emissions for the system as applied. It did, however, perform as well as or better than the standard in almost all cases.

- Thus, as a result of the severity of this evaluation test, not only would implementation of all of these alternative coating systems, over time, reduce emissions but these systems would also excel in the field under light or moderate conditions as compared to the standard coating system.

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SOLVENTLESS AND LOW-VOC ARCHITECTURAL COATINGS FORMULATED FROM NOVEL LATEXES WITH LOW MFT AND HIGH TG

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INTRODUCTION

In order to meet requirements of the Clean Air Act Amendments of 1990 and subsequent government legislation, coatings manufacturers must develop technologies allowing the formulation of low volatile organic compounds (VOCs)/low odor products that possess desirable end-use properties. The demands for change are both a challenge, and an opportunity for coating industries[1-7].

A common ideology of the coatings industry is that performance of solventless architectural coatings must be poor since they lack conventional coalescing agents. Indeed, it is well established that useful protective coatings must possess below ambient minimum film formation temperatures (MFT or MFFT) for flow, leveling, and substrate adhesion, **and** reach a glass transition temperature (T_g) well above ambient for a useful lifetime. While the synthesis of low MFT polymers alone is a relatively simple matter, the combination of low MFT and high T_g has been elusive for some time. The common problem associated with low MFT latexes is low film T_g and therefore poor performance properties. To overcome this dilemma, most contemporary water-based coatings are formulated from latexes with high MFT, and consequently require co-solvents and coalescing agents to facilitate film formation such that significant VOCs are present.

The focus of this work has concentrated on the design, synthesis, characterization, and formulation of novel low temperature MFT latexes that cured to above ambient T_g polymers. Consequently, emulsion polymers with T_g-MFT differentials approaching 20 ± 3°C have been synthesized and coating film properties formulated from the novel latexes are compared with those derived from a well-known commercial latex requiring coalescing agents.

EXPERIMENTAL DETAILS

Chemicals

Butyl carbitol (99+%) and propylene glycol (99%) were purchased from Aldrich, sodium bicarbonate (A.C.S. grade) from Fisher Scientific, potassium tripolyphosphate (KTPP, 94%) from

Pfaltz & Bauer, and Tronox CR-800 (rutile titanium dioxide pigment) from Kerr-McGee. Ti-Pure R900 (rutile titanium dioxide pigment) was obtained from DuPont, Huber 70C (Kaolin clay) from JM Huber, Beavewhite 325 (TALC) and Duramite (calcium carbonate) from ECC, Natrosol Plus (grade 330, an associative cellulosic thickener) from Aqualon, Kathon LX (1.5%, solventless microbicide), Tamol 731 (25%, polyacrylic acid dispersant), Ropaque OP-62 LO (36.5%, polymeric pigment), and QR-708 (35%, rheology modifier) from Rohm & Haas, UCAR Polyphobe 102 and 107 (25%, associative thickeners), and commercial latex (CL, 55% vinyl acrylic latex), Surfynol 465 (65%, nonionic surfactant, VOC content < 0.01%) from Air Products, and Byk 034 (defoamer, VOC content <2%) and Byk 035 (defoamer, VOC content <3%) from Byk. All ingredients were used as received.

Emulsion Polymerization

Starve-fed emulsion copolymerizations were used to synthesize solventless latexes of 40-50% solids content. The latexes have remained stable at room temperature for 10 months from this writing.

Emulsion Polymer Characterization

Latex properties have been determined and are listed in Table 1, together with those of a well-known vinyl acrylic latex. The solids contents were determined gravimetrically, while particle sizes were measured by a Coulter N4 MD Sub-micron Particle Analyzer. A Mettler DSC-30 measuring cell was used to determine T_g of the latex films (mid-point value). In a typical measurement, the temperature range for DSC analysis was from -50°C to 250°C at a heating rate of 10°C/min. Minimum film forming temperature of latexes was determined by a MFFT Bar 90.

Table 1. General Properties of Latex Paint Formulations

Latex Code	USM Latex A	USM Latex B	Commercial Latex (CL)[a]
Solids content (%)	45	42.5	55
pH	4.9	5.1	5.0
Dn (nm)	180	190	330
T_g (°C)	16.9	21.8	12
MFT (°C)	-1	2	8

[a]Technical data obtained from manufacturing specifications.

Latex Paint Formulations

A mill base for each latex of Table 1 was prepared according to the formulations in Table 2. The formulation recipes for

vinyl-acrylic paints at 55% PVC derived from the mill base **a** are listed in Table 3, while the formulation recipes for 20% PVC acrylic paints from mill base **b** are itemized in Table 4. Table 5 contains formulations from mill base **c** and QR-708 or Natrosol Plus thickeners formulated to 55% PVC.

Coating Film Characterization

Tensile strength and percent elongation of films were determined with an 810 Material Test System. The coatings were cast onto polyethylene sheets which allowed easy film removal. The test specimen were approximately 13 mm wide, 0.06-0.12 mm thick with a gauge length of 15 mm. Film dry times were determined from a 7-mil wet film on standard Leneta charts via a Gardner Circular Dry Time Recorder. Pencil hardness was measured according to American Society of Testing and Materials method (ASTM) standard D-3363, while the conical mandrel flexibility was determined via ASTM method D-522. Crosshatch adhesion tests were performed according to ASTM standard D-3359 on chromate pretreated aluminum plates and phosphatized steel plates. Scrub resistance was conducted on coated panels (PC-P121-10N, black plastic) after one and four weeks dry time, respectively, to obtain the number of cycles to initial break or to film failure with a 10-mil brass shim, according to ASTM standard D-2486. Specular gloss at 20°, 60°, and 85° was determined with a Byk-Gardner Micro Triglossmeter, while contrast ratios were measured with a Chroma-QC quality control system. Film thickness was determined by a Gardner Minitest 4000 Coating Thickness Gauge.

Table 2. Formulations for Mill Bases **a**, **b** and **c**[a]

Ingredients	Base **a**	Base **b**	base **c**	Suppliers
Tronox CR-800 (g)	455	1200	0	Kerr-McGee
Ti-Pure R900 (g)	0	0	1200	DuPont
Huber 70C (g)	292.5	0	0	JM Huber
Beavewhite 325 (g)	260	0	0	ECC
Duramite (g)	325	0	0	ECC
Natrosol Plus (g)	12	5	0	Aqualon
Kathon LX 1.5% (g)	5	4	4	Rohm & Haas
KTPP (g)	6.5	5	5	Pfaltz & Bauer
Byk 034 (g)	12	9	9	Byk
Tamol 731 25% (g)	39	30	30	Rohm & Haas
Surfynol 465 (g)	0	4	4	Air Products
Deionized Water (g)	715	500	498	
Total	2122	1757	1750	

[a]Ingredients were added at 800 rpm and mixed at 3500 rpm for 20 min.

RESULTS AND DISCUSSION

While the synthesis and composition of the solventless vinyl acrylic latexes cannot be disclosed at this time, it is instructive to examine the properties of formulated coatings. The T_g-MFT differential (Table 1) of the commercial latex is 4°C, while the differential for USM latex A and USM latex B is 18°C, and 20°C, respectively. T_g values were determined from clear films that had air-dried for two weeks. These data are suggestive of ambient temperature crosslinking. For instance, the films were immersed in THF and have remained intact, clear, and non-cloudy after 3 months as of this writing.

Table 3. Formulations of Vinyl Acrylic Paints of 55% PVC from Mill Base **a**

Paint Code[a]	USM A-**a**	USM B-**a**	Commercial CL-**a**	Suppliers
Mill Base **a** (g)	180	180	180	This work
Deionized Water (g)	29.5	22	36	
Na2CO3 (20%) (g)	6.0	7.0	6.0	Fisher
Byk 035 (g)	0.4	0.4	0.4	Byk
Surfynol 465 (g)	1.0	1.0	1.0	Air Products
USM Latex A (45%) (g)	86.7	0	0	This Work
USM Latex B (42.5%) (g)	0	91.8	0	This work
Commercial Latex (55%) (g)	0	0	71.0	
Ropaque OP-62 LO (36.5%) (g)	20	20	20	Rohm & Haas
Polyphobe 107 (25%) (g)	0.8	1.2	1.3	Union Carbide
Polyphobe 102 (25%) (g)	5.0	6.0	6.4	Union Carbide
Butyl Carbitol (g)	0	0	3.0	Aldrich
Propylene Glycol (g)	0	0	7.0	Aldrich
Total	329.4	329.4	332.1	
Paint Properties				
PVC (%)	55	55	55	
Volume Solids (%)	33.6	33.0	33.5	
Weight Solids (%)	49.9	50.0	49.6	
Stormer Viscosity (KU)	99	100	105	
ICI (poise)	1.6	2.0	2.0	
pH, Initial	9.1	9.4	8.6	
VOC (g/L)	<0.4	<0.4	122	

[a]Latex name - mill base code.

Table 4. Formulations of Vinyl Acrylic Paints of 20% PVC from Mill Base **b**

Paint Code[a]	USM A-**b**	USM B-**b**	Commercial CL-**b**	Suppliers
Mill Base **b** (g)	100	100	100	This work
Deionized Water (g)	35.3	25.3	58.0	
Na2CO3 (20%) (g)	8.4	8.0	8.0	Fisher
Byk 035 (g)	0.4	0.4	0.4	Byk
Surfynol 465 (g)	1.6	1.6	1.6	Air Products
USM Latex A (45%) (g)	170	0	0	This work
USM Latex B (42.5%) (g)	0	179	0	This work
Commercial Latex (55%) (g)	0	0	138	
Polyphobe 107 (25%) (g)	1.0	1.0	1.3	Union Carbide
Polyphobe 102 (25%) (g)	7.0	7.0	11.0	Union Carbide
Butyl Carbitol (g)	0	0	3.0	Aldrich
Propylene Glycol (g)	0	0	7.0	Aldrich
Total	323.7	322.3	328.3	
Paint Properties				
PVC (%)	20	20	20	
Volume Solids (%)	33.0	33.0	32.6	
Weight Solids (%)	46.3	46.4	45.6	
Stormer Viscosity (KU)	83	78	81	
ICI (poise)	1.3	1.0	1.3	
pH, Initial	8.8	9.3	8.1	
VOC (g/L)	<0.3	<0.3	118	

[a]Latex name-mill base code.

Table 5. Formulations of Vinyl Acrylic Paints of 55% PVC from Mill Base **c**

Paint Code[a]	USM A-**c**-1	USM A-**c**-2	USM B-**c**	Suppliers
Mill Base **c** (g)	200	200	200	This work
Natrosol Plus[b] (3.5%) (g)	30.1	0	0	Aqualon
QR-708[c] (7%) (g)	0	17.8	17.6	Rohm & Haas
Na2CO3 (20 %) (g)	4.2	3.8	3.8	Fisher
Surfynol 465 (g)	0.9	0.9	0.9	Air Products
Byk 035 (g)	0.4	0.4	0.4	Byk
USM Latex A (45%) (g)	72.3	72.5	0	This work
USM Latex B (42.5%) (g)	0	0	76.6	This work
Total	307.9	295.4	299.3	
Paint Properties				
PVC (%)	55	55	55	
Volume Solids (%)	33	34.0	33.3	
Weight Solids (%)	56.0	58.3	57.6	
Stormer Viscosity (KU)	76	83	80	
ICI (poise)	0.8	1.1	1.0	
pH, Initial	8.4	8.6	8.8	
VOC (g/L)	<0.51	22.5	22.3	

[a]Latex name-mill base code - numerical number if applicable.

[b]Pre-mixed at 500 rpm to obtain 3.5% Natrosol Plus (grade 330) water solution.

[c]140 g of QR-708 (35%) was diluted in 560 g of water and pre-mixed, containing 7.8% of propylene glycol.

USM vinyl acrylic latexes and the commercial latex were formulated into paints at 55 and 20% PVC according to the formulations of Table 3 (mill base **a**) and Table 4 (mill base **b**), respectively. A formulation above the critical pigment volume concentration (CPVC) was chosen, even though some suggest formulating below CPVC for solventless coatings[8]. The CPVC was approximated by determining an oil absorption of 24.3 g/L for mill base **a** according to ASTM D-281. Although an approximate CPVC of 54.8 was calculated, the true CPVC is less since the oil absorption technique gives values greater than those for latex paints, a result of lower binder efficiencies of the lattices[9,10].

USM vinyl acrylic lattices were formulated at 55% PVC using Natrosol Plus or QR-708 as thickener rather than UCAR Polyphobes as noted in Table 5. This approach was undertaken since the rheology modifier QR-708 contains 7.8% propylene glycol and contributes to VOC. Small amounts of propylene glycol were added to the formulation to study, and thus better appreciate, the

performance of solventless USM latexes in low VOC coatings as well as solventless coatings.

Paints produced according to Tables 3, 4, and 5 formulations were made into films for film property determinations. All film properties of Tables 6-8 were determined after 7 days air dry. Films used for tensile and elongation tests were of 16-mil wet film thickness, while the remaining films were of a 7-wet mil thickness.

Paint film coalescence is crucial to developing film properties, and the efficacy of film formation was estimated from tensile property measurements. As shown in Tables 6 and 7, all films prepared from solventless paints were much stronger than their counterparts, the films derived from paints of CL.

Table 6. Film Properties Vinyl Acrylic Paints Formulated from Mill Base **a**

Paint Code	USM A-**a**	USM B-**a**	Commercial CL-**a**	ASTM Method #
Tensile Strength (psi)	853	884	596	D-2370
Elongation at Break (%)	8.4	8.6	26.1	D-2370
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.6	33.0	33.5	
Dry Time (min)	50	40	55	D-1640
MFT (°C)	0	0.5	1	D-2354
Pencil Hardness	4H	4H	2H	D-3363
Conical Mandrel (1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	5B	5B	4B	D-3359
Adhesion on Steel	5B	5B	4B	D-3359
Scrub				
Initial Break	170	160	170	D-2486
Film Failure	240	230	250	D-2486
Sheen, 85°	1.9	1.9	1.7	D-523
Contrast Ratio	94.8	94.9	94.1	D-3022

The dry time for solventless paints was consistently shorter than for conventional paints. Also, films from the solventless coatings were typically harder after 7 days dry (Tables 6, 7 and 8). All paint films changed little after the 7 days air dry period as noted by pencil hardness determinations (Table 9).

A determination of MFTs for all paints, solventless and low-VOC systems were similar and in the 0-2°C range.

Table 7. Film Properties Vinyl Acrylics Coatings Formulated from Mill Base **b**

Paint Code	USM A-**b**	USM B-**b**	Commercial CL-**b**	ASTM Method #
Tensile Strength (psi)	468	821	245	D-2370
Elongation at Break (%)	717	403	1130	D-2370
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.0	33.0	32.6	
Dry Time (min)	45	55	60	D-1640
MFT (°C)	2	2	2	D-2354
Pencil Hardness	F	H	HB	D-3363
Conical Mandrel (1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	5B	5B	4B	D-3359
Adhesion on Steel	5B	5B	4B	D-3359
Scrub				
Initial Break	700	600	400	D-2486
Film Failure	860	720	530	D-2486
85° Gloss	82.8	79.5	85.3	D-523
60° Gloss	70.4	66.6	73.0	D-523
20° Gloss	31.9	22.9	28.8	D-523
Contrast Ratio	97.2	97.2	95.7	D-3022

Wet and dry adhesion values for USM lattices derived coatings applied to aluminum and steel panels were superior to coatings formulated with commercial lattices. Conventional latex paints have long suffered from wet adhesion limitations by virtue of being stabilized in, and delivered from water[11]. Thus, techniques to evaluate the hydrophobicity of paint films are significant to paint performance, and scrub resistance tests are therefore a common practice. In the present circumstance, scrub resistance values (Tables 6, 7, and 8) of the solventless, coalescent-free, paints are comparable with conventional formulations.

Table 8. Film Properties Vinyl Acrylic Coatings Formulated from Mill Base **c**

Paint Code	USM A-**c**-1	USM A-**c**-2	USM B-**c**	ASTM Method #
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.0	34.0	33.3	
Dry Time (min)	30	35	40	D-1640
MFT (°C)	2	2	2	D-2354
Pencil Hardness	F	F	F	D-3363
Conical Mandrel(1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	4B	4B	4B	D-3359
Adhesion on Steel	4B	4B	4B	D-3359
Scrub				
Initial Break	200	240	190	D-2486
Film Failure	280	300	260	D-2486
85° Gloss	58.2	57.1	48.4	D-523
60° Gloss	13.5	13.3	14.3	D-523
20° Gloss	1.9	1.9	1.9	D-523
Contrast Ratio	98.5	98.6	98.0	D-3022

It has been suggested that the analytical methods for evaluating solventless coatings should be reviewed since no- and low-VOC coatings are new technology[2,3]. For instance, while conventional latex coating formulations possess added coalescing agents, it is reasonable to conclude that full coalescence, and thus film properties, would occur quickly. However, solventless latex coatings contain no added coalescing agents, and it is likewise reasonable that film property development would be delayed to some extent. Thus, scrub resistance of the lattices were evaluated at 7 and 28 day dry times, the latter being consistent with the DIN 53.778 standard scrub test used in Germany[3]. The results are plotted in Figures 1 and 2.

Flat paints (55% PVC) (Figure 1) are heavily pigmented and are not expected to equal the performance of the less pigmented semi-gloss coatings (20% PVC) (Figure 2). Indeed, this is confirmed for all coatings of Figures 1 and 2, i.e., all 20% PVC coatings are superior in scrub resistance to the best 55% PVC formulation whether dried 7 or 28 days. The addition of small amounts of coalescing aids in formulas USM A-**c**-2 and USM B-**c** provide slight improvement in coalescence as reflected in improved scrub resistance after 7 days dry time. However, greatest improvement in scrub resistance was developed in the solventless coatings USM A-**a**, USM B-**a** and USM A-**c**-1 by simply extending the drying period from 7 to 28 days. This latter effect is clearly a result of the unique coalescence and curing mechanism of the USM lattices.

Table 9. Pencil Hardness as a Function of Dry Time

Paint Code	MFT °C	Thickness mils	Pencil Hardness (Scratch) 1 day	7 days	17 days
USM A-**a**	0	1.37	HB	4H	4H
USM B-**a**	0.5	1.51	F	4H	4H
CL-**a**	1	1.22	H	2H	2H
USM A-**b**	2	1.05	B	F	F
USM B-**b**	2	1.16	B	H	H
CL-**b**	2	1.13	B	HB	HB
USM A-**c**-1	2	1.28	HB	F	F
USM A-**c**-2	2	1.28	HB	F	F
USM B-**c**	2	1.39	HB	F	F

Gloss values demonstrate that the solventless coatings of Table 7 are effectively coalesced and are gloss competitive with the conventionally formulated coating. The lower gloss values are noted when Ti-Pure R900 is the lone pigment (Table 8).

CONCLUSIONS

Vinyl acrylic lattices have been synthesized that require no coalescing aids, and possess T_g-MFT differentials of 20 ± 3°C. The low MFT allows formulation of waterborne coatings that will film form near 0°C. Film properties have been evaluated and found to be equal or better than coatings formulated with VOC contributing coalescing aids.

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Figure 1. Scrub Resistance For Flat Wall Paints

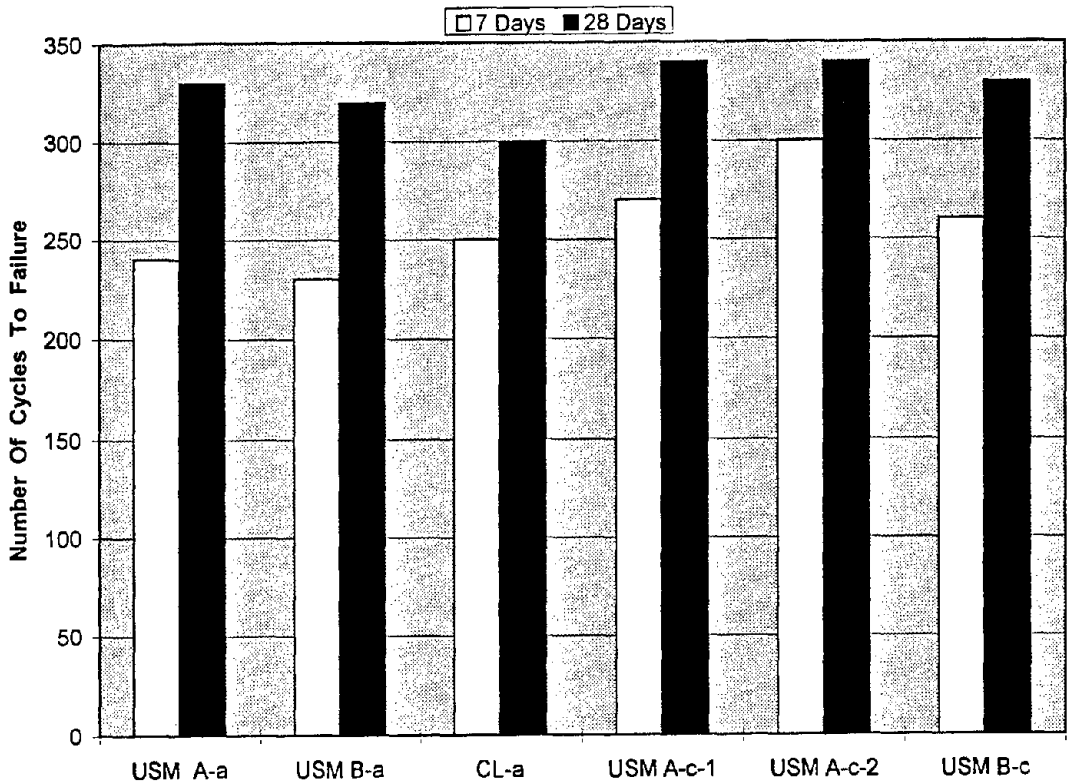
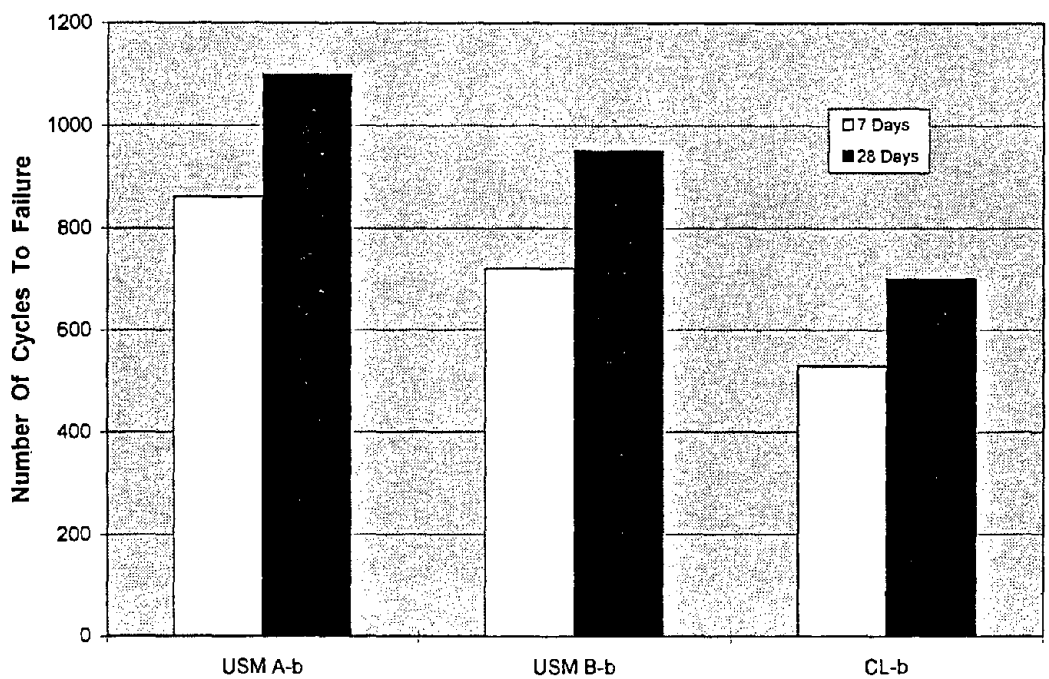


Figure 2. Scrub Resistance For Semigloss Paints



This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

EVALUATION OF EMISSIONS FROM LATEX PAINT

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INTRODUCTION

Traditional methods of assessing latex paint emissions have been developed to determine cumulative mass emissions of volatile organic compounds (VOCs) for purposes of determining their impact on the ambient air, specifically for their contributions to photochemical smog. In indoor environments, the concern is directed to determining the time varying exposure of occupants to total VOCs, as well as individual organic compounds. The Indoor Air Branch of EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, has developed a three phase approach (i.e., small chamber source characterization - indoor air quality (IAQ) modeling - test house validation) for developing emissions data for indoor sources (see Figure 1)[1]. This approach provides information on the temporal distribution of indoor emissions and allows occupant exposures to these emissions to be determined[2]. Over the past year, this approach has been used to evaluate indoor emissions from latex paint.

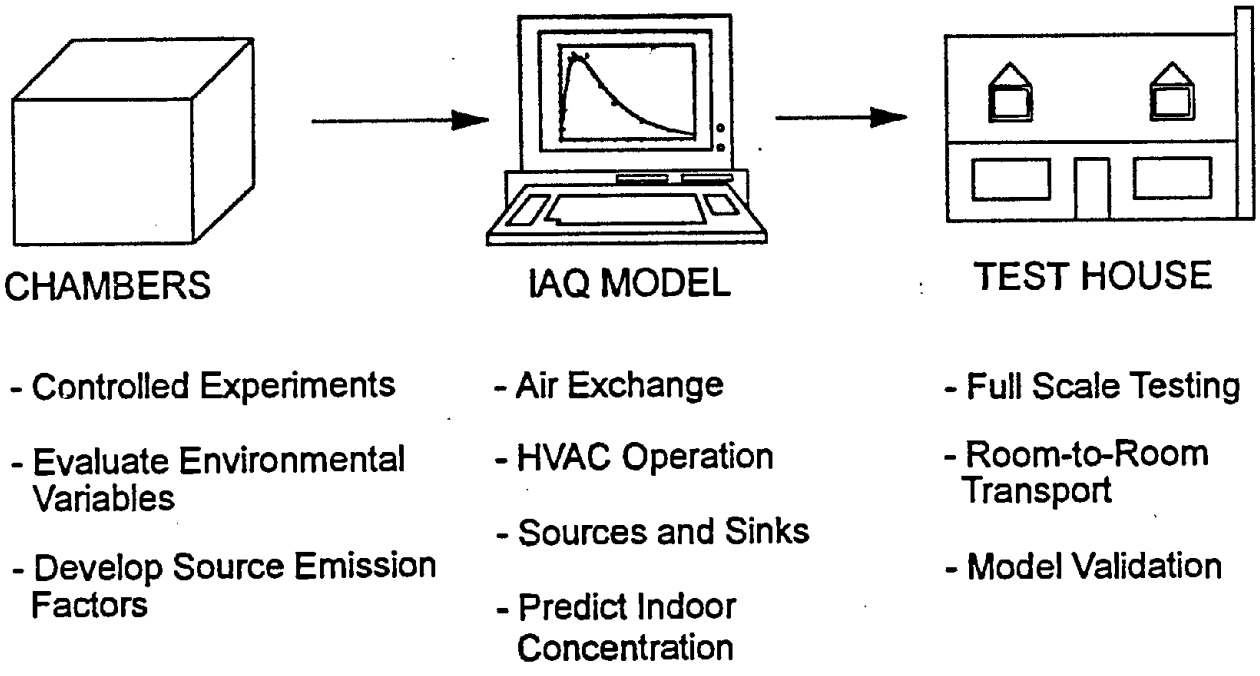

Figure 1. Three-phase IAQ research approach

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RESEARCH PLAN

A three-part latex paint emissions study is underway: 1) Initial Assessment; 2) Chamber Testing; 3) Test House Validation Studies. The *Initial Assessment* was designed to determine the most appropriate techniques for conducting the overall latex paint assessment program, including: a) selection and purchase of test paint; b) analysis of volatile organic compounds (VOC) and water content using American Society for Testing and Materials (ASTM) methods; c) determination of major organic compounds; d) development of optimal sampling and analysis methods for organic paint emissions; and e) evaluation of paint application methods. The purposes of the *Chamber Testing* are to: a) select the test substrate; b) develop data for determining VOC emission rates; and c) develop and evaluate source emission models, including mass transfer models. The *Test House Validation Studies* will develop data for evaluating and validating source emission models, including mass transfer models. In addition, the studies should provide data for assessing scale-up of small chamber source emissions data. The following information is expected to result from this assessment of latex paint: a) Emission rate data for VOCs from latex paint on gypsumboard for specific test parameters; b) Validated source emissions models for latex paint, including mass transfer models; and c) Test house data showing the concentrations of VOCs from latex paint. Ultimately, the effort should result in a test method proposal for ASTM.

The three part evaluation program was initiated in 1994. Part 1 (Initial Assessment) has been completed; Part 2 (Chamber Testing) is scheduled for completion early in 1995; and Part 3 (Test House Studies) will be completed by the end of 1995.

INITIAL ASSESSMENT

The purpose of the *initial assessment* was to determine the most appropriate techniques for conducting the overall latex paint assessment program, including: a) selection and purchase of test paint; b) compilation of information on paint composition based on product label and MSDS (Manufacturer's Safety Data Sheet); c) analysis of VOCs and water content using ASTM methods; d) determination of major organic compounds; e) development of optimal sampling and analysis methods for organic paint emissions; and f) evaluation of paint application methods.

Paint Composition

The paint selected for evaluation is a white interior flat latex wall paint (with vinyl acetate monomer) produced by a major US manufacturer. Based on ASTM methods[3] for paint analysis, the paint has the following composition by weight: non-volatiles = 57% and volatiles = 43% (water = 40% and VOC = 3%). Analysis of the paint by liquid injection to a gas chromatograph gave a total VOC (TVOC) content = 45 mg/g, with the following composition (in mg/g): ethylene glycol = 24; Texanol® = 13; butoxyethoxyethanol = 5; propylene glycol = 2; and diethylene glycol = 1.

Sampling and Analysis Methods

Evaluation of available methods resulted in the selection of the following sampling and analysis techniques for VOC emissions from latex paint: a) sampling on Tenax®TA sorbent; b) thermal desorption and concentration; and c) analysis by gas chromatograph (with a DB™-Wax column) using a flame ionization detector (FID).

Paint Application Methods

Three application methods were evaluated: slit applicator (a laboratory "standard" method), brush, and roller. The roller method was selected for use in the remainder of the study.

CHAMBER TESTING

Environmental test chamber methods have been developed for evaluating emissions from indoor materials and products[4]. Flow-through, dynamic chambers are used when emission rates are to be determined. The chambers used in this study have a volume of 53 liters and are constructed with electropolished stainless steel interior surfaces to minimize adsorption of VOCs. Small fans are used to enhance mixing and provide a velocity near the test surface of 5 - 10 cm/s, which is typical of indoor environments. Emissions testing is conducted by placing a freshly painted (2 - 3 min.) substrate (16.3 x 16.3 cm) in the chamber, painted side up. The chamber is then closed, and clean air ($< 5\ \mu g/m^3$ TVOC) flow is started through the chamber. A flow rate of 0.44 l/min, equivalent to 0.5 air changes per hour, is used. Samples of the chamber outlet are taken using the techniques described above. Sufficient samples are collected to describe the change in emissions over time. Testing is conducted at 23°C with an inlet relative humidity of 50%.

The purpose of the *chamber testing* is to: a) Select the test substrate; b) Determine emission rates for total VOC as well as for individual compounds; c) Determine the effect of previous coats on emissions; d) Determine short- and long-term emission rates; and e) Evaluate and develop source emission models, including mass transfer models.

Selection of Test Substrate

VOC emissions from painted gypsumboard and stainless steel were evaluated using dynamic chamber tests. While stainless steel is routinely used as a test substrate in emissions testing due to its non-adsorbent properties, gypsumboard is a more realistic choice for latex paint. As shown in Figure 2, VOC emissions from painted gypsumboard are quite different than those from stainless steel. Significant amounts of VOCs are adsorbed by the gypsumboard, thus reducing the short term emissions to the indoor air. Thus, gypsumboard was selected at the test substrate.

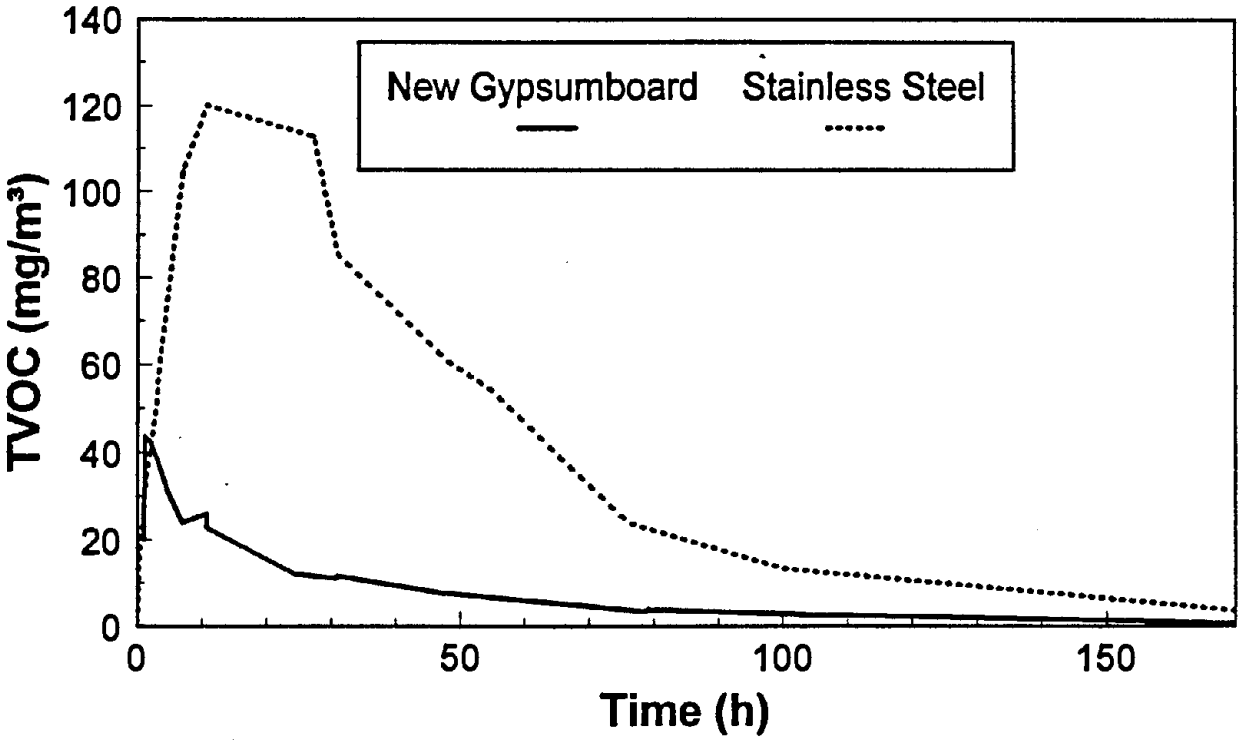


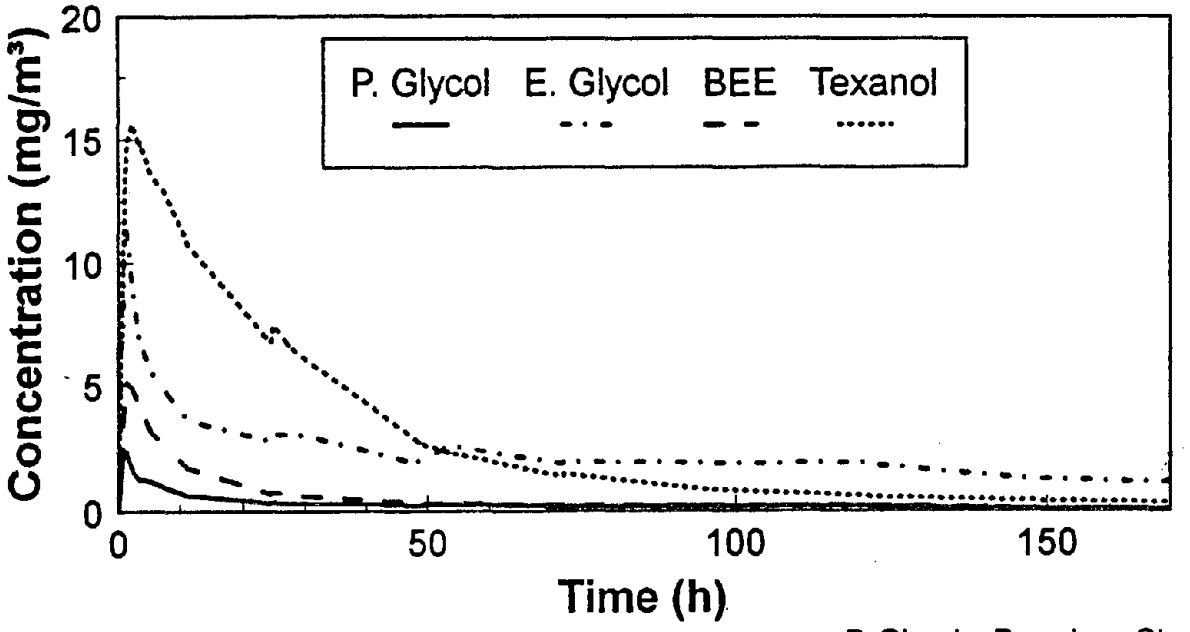
Figure 2. Emissions of TVOC from painted gypsumboard and stainless steel (Dynamic chamber tests)

Emissions of Individual Latex Paint VOCs

The chamber samples were also analyzed to determine the emissions of individual latex paint components, namely: ethylene glycol, propylene glycol, diethylene glycol, butoxyethoxyethanol, and Texanol® [2,2,4-Trimethyl-1,3-pentanediol Mono(2-methylpropanoate); mixture of two isomers]. As shown in Figure 3, emissions of Texanol® and ethylene glycol are the highest, with Texanol® emissions predominating for the first 50 hours and ethylene glycol emissions being the primary VOC emitted thereafter.

The Effect of Previous Coats on Emissions

Testing was conducted to determine if paint applied to previously painted gypsumboard affects the emission profile. Two previously coated boards were used: 1) a piece of gypsumboard cut from a wall of EPA's IAQ test house that had not been repainted for over 8 years and 2) a gypsumboard sample painted 5 weeks previously. As shown in Figure 4, the two previously painted gypsumboards had emission profiles essentially the same as for the first coat on new gypsumboard.



P. Glycol = Propylene Glycol
E. Glycol = Ethylene Glycol
BEE= Butoxyethoxyethanol

Figure 3. Emissions of latex paint VOCs from painted gypsumboard (Dynamic chamber test)

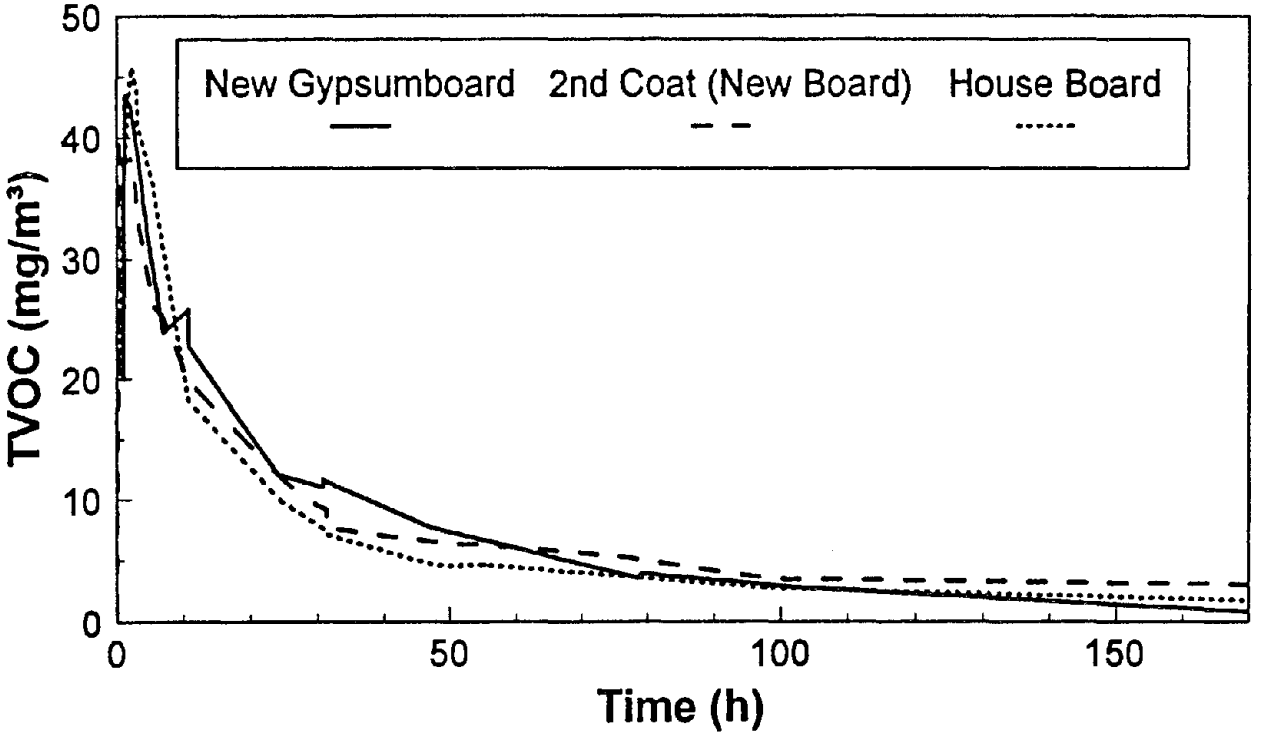


Figure 4. Emissions of TVOC from first and second coats of latex paint on gypsumboard (Dynamic chamber tests)

Long and Short Term Emissions

Many wet, evaporative sources of indoor air pollution emit for only a short time (e.g., several days). Most of the testing done in this evaluation program occurred over a 7 day (168 hour) period, as shown in Figures 2, 3, and 4. One test has been continued in order to observe the emissions from latex paint over the long term. Figure 5 shows the emissions of VOCs over a period of almost 6 months (4200 hours or 175 days). Note that the emissions of ethylene glycol are much higher than the other compounds. Also note that at the last sampling period, the concentrations of butoxyethoxyethanol and Texanol® were near the quantification limit of the sampling and analysis system.

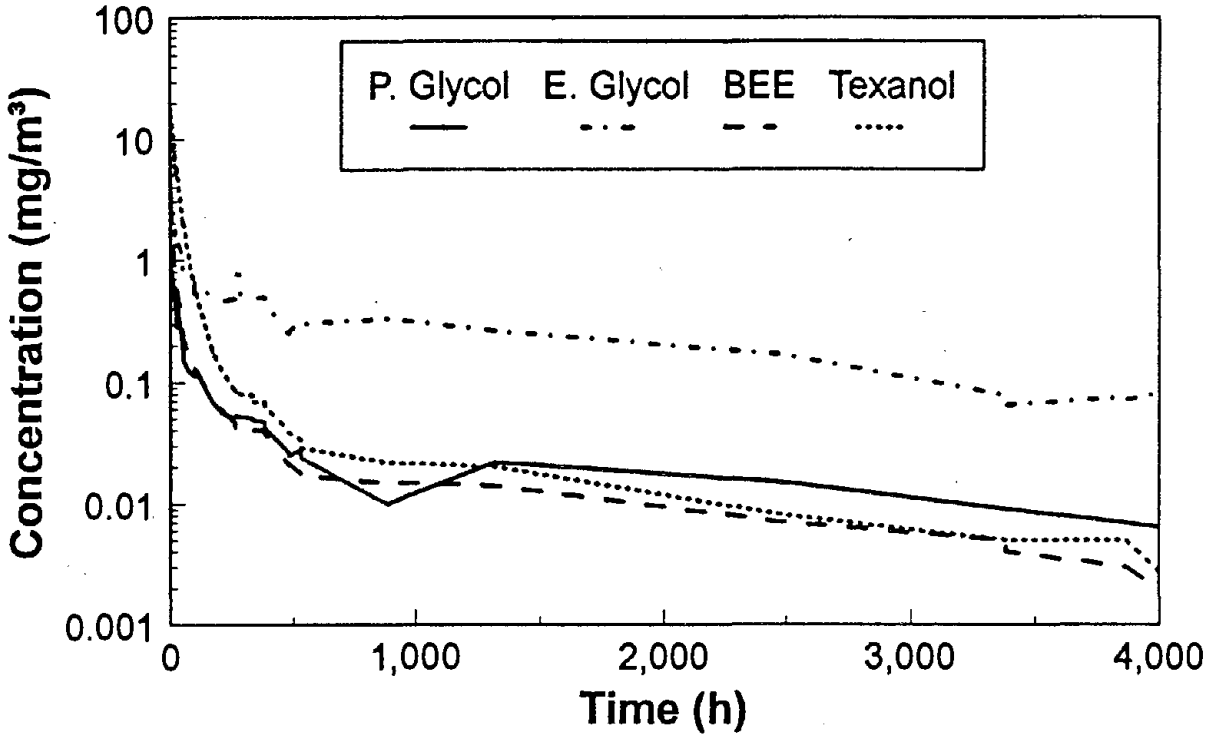


Figure 5. Long term emissions of latex paint VOCs from painted gypsumboard (Dynamic chamber test)

Source Emission Models

As discussed, dynamic chamber testing is the most common method being used to determine indoor source emission rates. Both empirical models and fundamental mass transfer models are being developed to predict the emission rates of sources.[5] Source emission factors are determined by fitting appropriate source models to chamber concentration vs. time data. The model selected is based on the source emissions profile over time.

For sources with decaying emissions, a common approach is to assume a first order decay:

$$EF = EF_o e^{-kt} \quad (1)$$

where EF_o = initial emission factor (mg/m^2h); k = first order rate constant (h^{-1}); and t = time (h). Some decaying sources, usually long lasting emitters, can be described by a second order decay equation:

$$EF = (EF_o)/(1 + k_2 EF_o t) \quad (2)$$

where k_2 = second order decay constant.

Source models have also been developed that are based on fundamental mass transfer processes. For sources with gas-phase limited mass transfer (e.g., evaporation from wet sources), the emission factor can be described as:

$$EF = k_g(C_s - C) \quad (3)$$

where, k_g = mass transfer coefficient (m/h); C_s = concentration of vapor in the air just above the emitting surface (mg/m^3); and C = concentration of vapor in the room air (mg/m^3). C_s is the vapor pressure, expressed as concentration, in equilibrium with the source. Previous work[5] has shown a linear relationship between C_s and the mass of VOC in the source (M):

$$C_s = C_v(M/M_0) \quad (4)$$

where C_v = concentration of VOC over fresh source (i.e., at time = 0); M = mass in source (mg/m^2) at time t; M_0 = initial mass in source (mg/m^2). The mass transfer coefficient (k_g) is determined by the vapor diffusivity of the emissions in air, the velocity above the source, and the geometry (size and shape) of the source.

Data from the dynamic chamber testing of painted gypsumboard have been fit with several source emissions models. As shown in Figure 6, the first order decay model (Equation 1) does not apply to latex paint TVOC emissions, while the gas-phase mass transfer model (Equations 3 & 4) does a good job of predicting short term emissions. Long term emissions are mainly controlled by diffusion within the gypsumboard, so a gas-phase limited model will not provide adequate predictions. Figure 7 illustrates the use of a second order decay model (Equation 2) for predicting long term emissions. A mass transfer model embodying both gas- and solid-phase mass transfer controls is under development.

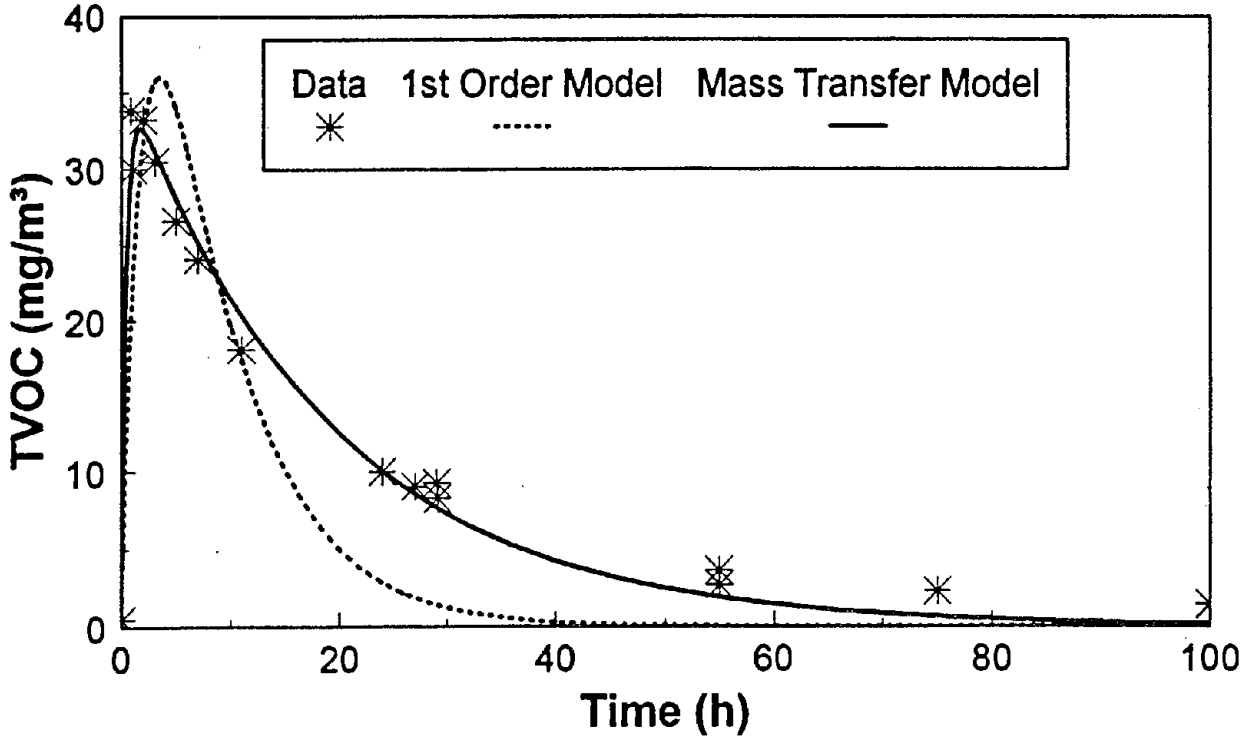


Figure 6. Short term emissions models - TVOC from painted gypsumboard (Dynamic chamber test)

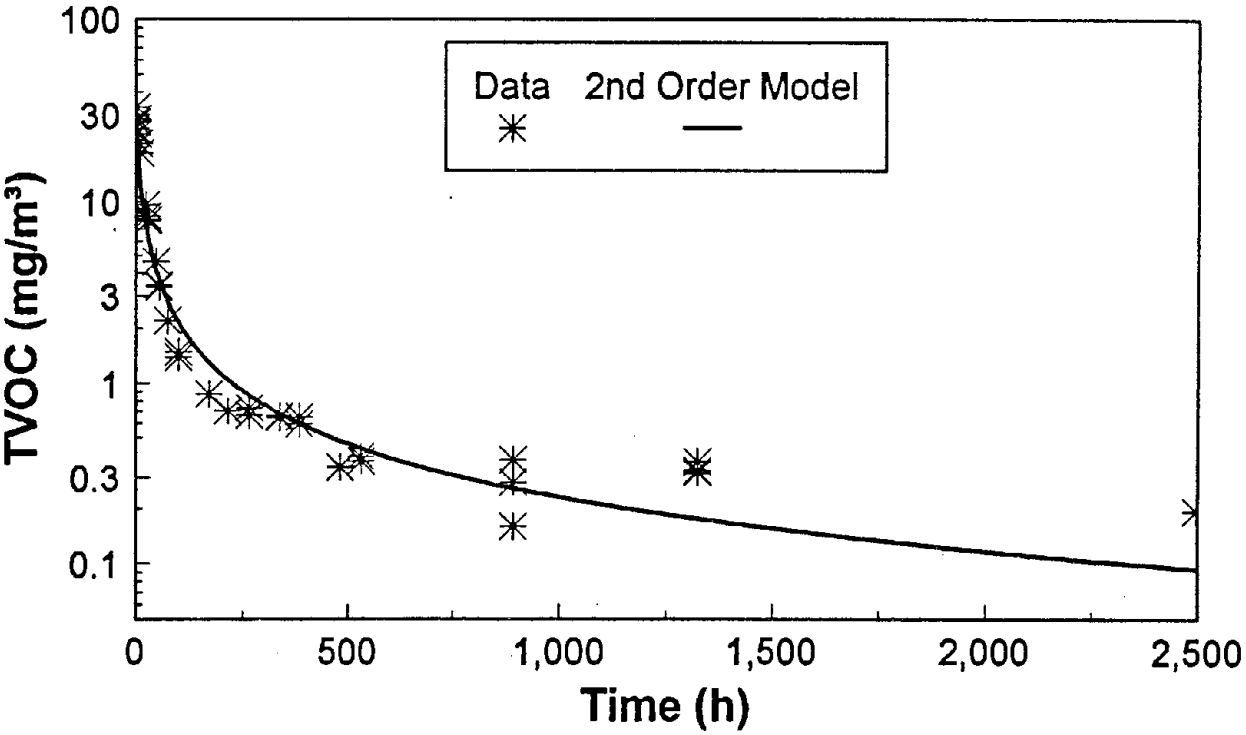


Figure 7. Long term emission model - TVOC from painted gypsumboard (Dynamic chamber test)

TEST HOUSE VALIDATION STUDIES

The purpose of the *test house validation studies* is to develop data for evaluating and validating source emission models, including mass transfer models. In addition, the studies should provide data for assessing scale-up of small chamber source emissions data. Test house studies will include: a) Anemometer traverses of test house walls to determine velocity distributions; b) Experiments to validate source emission mass transfer models; and c) Development of mass transfer coefficients for typical painting scenarios.

APPLICATION OF RESEARCH RESULTS

Emission rates developed from source testing are used in indoor air quality models[6] to predict indoor concentrations over space and time. The second order emission model (Equation 2 and Figure 7) was used to predict the concentrations of TVOCs in a hypothetical three-room apartment (see Figure 8) when latex paint is applied to interior walls.

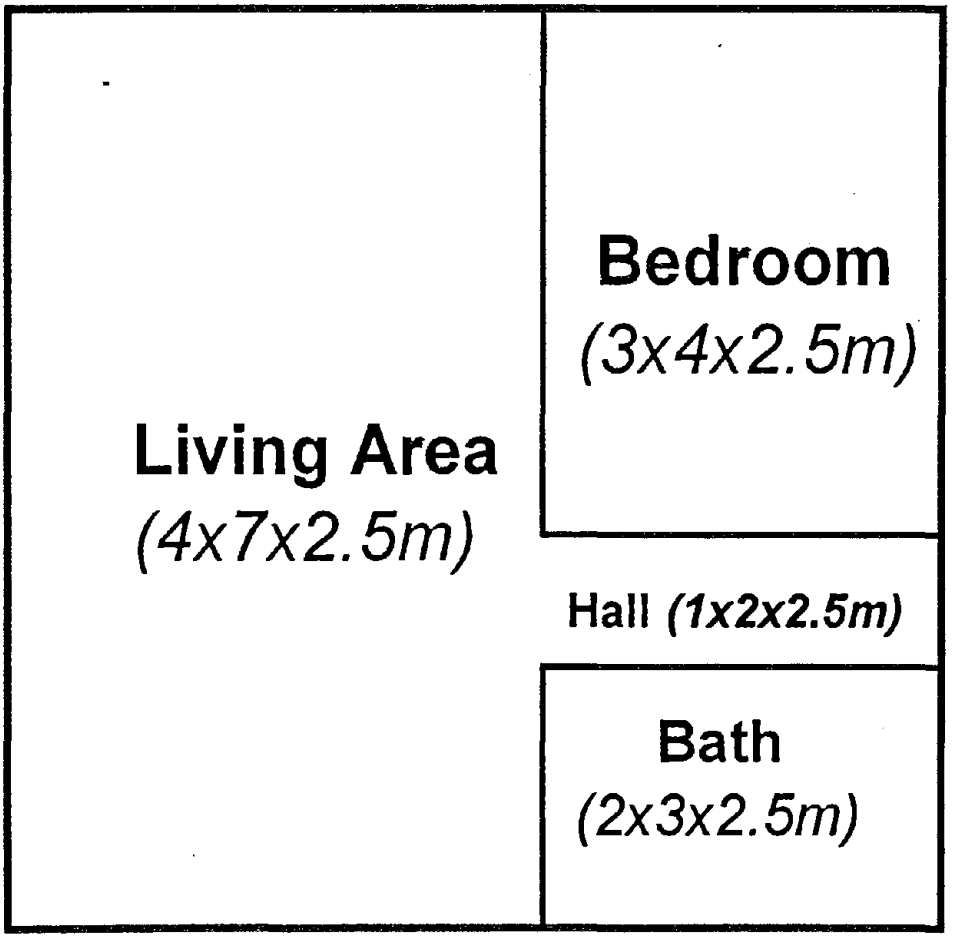


Figure 8. Floor plan for one-bedroom apartment

The model used an outdoor air exchange rate of 0.5 per hour and assumed a forced air heating/cooling system. The painting schedule was: Living area, 8AM - Noon; Hall, 1 - 2PM; Bedroom, 2 - 3PM; and Bath, 3 - 4PM. Figures 9 and 10 show the concentrations in each room for TVOC and Texanol®, respectively, for the first 100 hours. After that time, the concentration in all rooms was equal and the decay was much slower. Figure 11 shows the concentration of TVOC in the living area out to 700 hours.

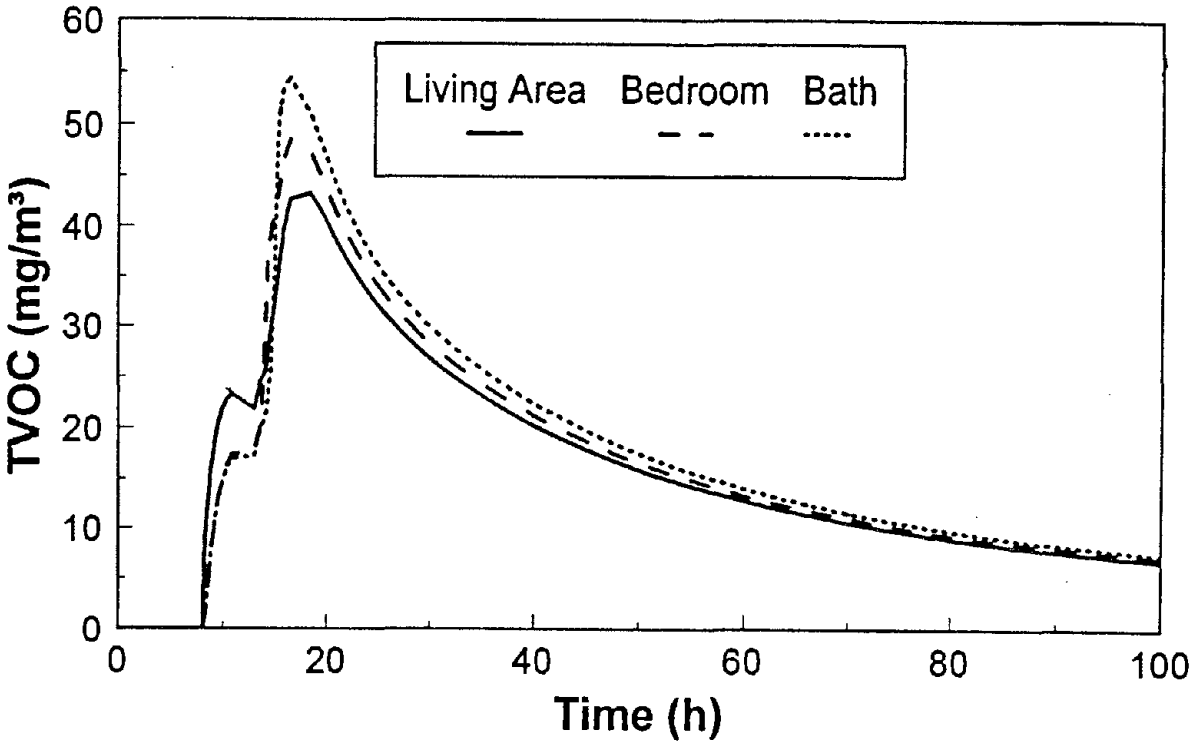


Figure 9. Predicted concentrations of TVOC from interior painting

FINAL PRODUCTS

The following information is expected to result from this assessment of a latex paint: a) Emission rate data for VOCs from latex paint on gypsumboard for specific test parameters; b) Validated source emissions models for latex paint, including mass transfer models; c) Test house data showing the concentrations of VOCs from latex paint; and d) A draft ASTM "Standard Practice for Determining Emissions from Interior Latex Paints." If a mass transfer model can be used to successfully predict emissions, a test method based on ASTM VOC content and equilibrium data from static headspace should be possible. Thus, the dynamic chamber test method would be replaced by a simpler and less expensive technique. Other latex paints need to be evaluated to provide data for generalizing these test methods.

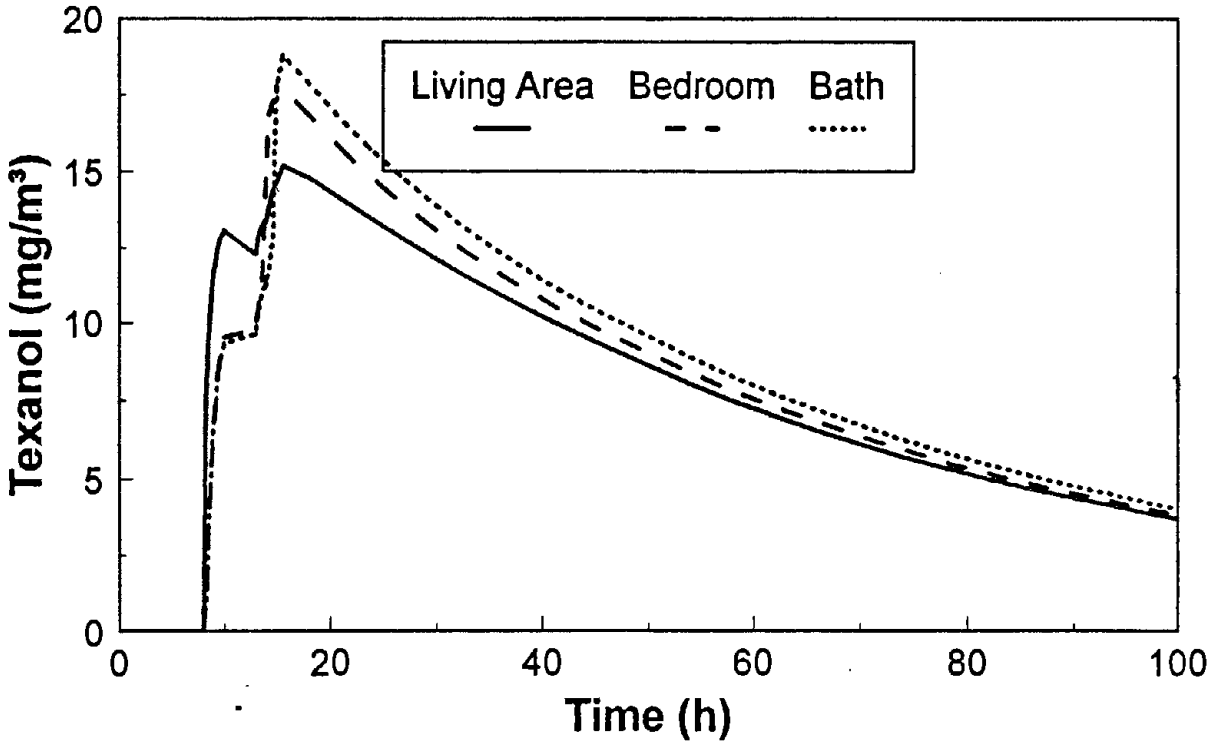


Figure 10. Predicted concentrations of Texanol® from interior painting

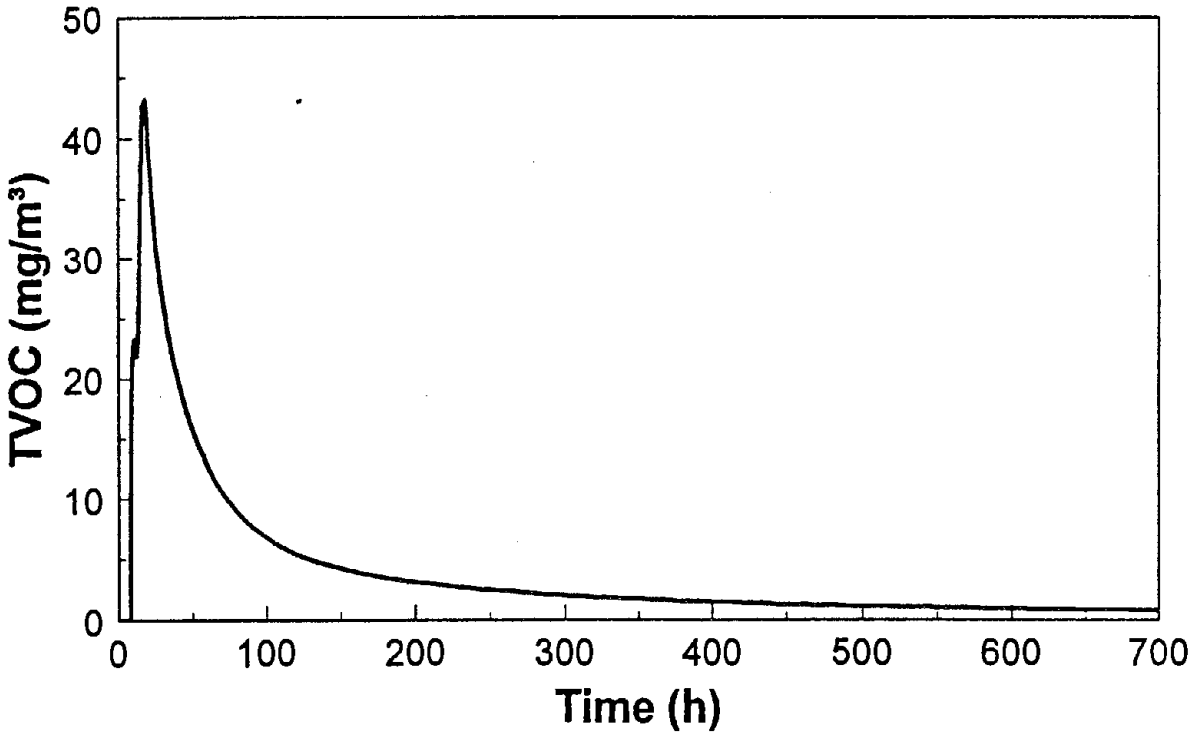


Figure 11. Predicted TVOC concentrations in living area from interior painting

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New Polyurethane Prepolymers for Ultra-Low VOC Plural Component Coatings

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SUMMARY

The drive toward lower and lower VOC coatings has led to a resurgent interest in plural component spray application technology. With this equipment, the reactive components are mixed just before or at the spray gun. Separating the components in this way before spraying allows the use of elevated temperatures to reduce formulation viscosity without concerns over the working life of the formulation, reducing or eliminating the need for solvent. The development of a new technology for producing very narrow molecular weight distribution isocyanate-terminated prepolymers with very low residual diisocyanate monomer has improved the viability of this process. These prepolymers decrease rapidly in viscosity with increasing temperature, and the low monomer content reduces worker exposure potential. This paper will introduce this prepolymer technology and illustrate the use of these prepolymers in formulating very low or near zero VOC polyurethane topcoats for high performance applications.

INTRODUCTION

Two part solvent-based coatings systems utilizing aliphatic isocyanates and polyester or acrylic polyols have become the industry standard for weatherable topcoats. These coatings systems combine exceptional resistance to chemical and physical damage with high gloss levels and long term retention of gloss, color and mechanical properties. Traditionally, these coatings systems have been formulated with a liquid polyisocyanate as one component and a high molecular weight, high functionality polyol and associated pigments and additives as the second component.[1]

A major driving force in the reformulation of coatings the world over is the need to reduce solvent emissions on application. One disadvantage of these traditional polyurethane formulations is the high solvent demand of the polyol component. This factor has limited the volatile organic content (VOC) reduction available with traditional polyol systems. One route to lowering VOC is to employ lower molecular weight polyols. As formulators incorporate more and more lower molecular weight (lower viscosity) polyols or reactive diluents into their systems, there has been an inevitable trade-off in physical properties of the resulting coatings and/or handling of the reactive mixture. Many low VOC polyurethane coatings today suffer from poor solvent resistance, poor flexibility, and an extreme sensitivity to catalyst level as it affects cure profile. In addition, with less solvent in the formulation and fewer ingredients to manipulate, maintaining convenient mixing ratios has also been a struggle.

Isocyanate producers have done an excellent job in educating their customers on the safe use of isocyanates in coatings and are constantly working to lessen any potential problems associated with these materials. One approach toward further improving isocyanate handling, described here, is to utilize higher molecular weight, isocyanate-terminated prepolymers as a source of isocyanate.

Concurrent with the drive toward lower and lower VOC for conventionally applied coatings, formulators and applicators have also increased the use of more specialized application equipment. Plural component application equipment has been used for many years to apply 100% reactive, fast reacting polyurethane coatings for thick film linings and for adhesives and

sealants. With this equipment, the reactive components are metered into a chamber designed to rapidly mix the components. The reactive mixture is then pumped to a traditional airless or air-assisted airless spray gun.

This process has a number of advantages over conventional application equipment. Since material is used only on demand, little product is wasted, and start-up and shut-down times are reduced. In fact, for reasons of the productivity enhancement alone seen with this equipment, product finishers have sharply increased their use of plural component polyurethane coatings on industrial finishing lines. Often traditional solvent-borne, lower VOC coatings are used with increased catalyst levels to speed cure times and lower oven temperatures. Since the reactive components are mixed only seconds before application, short potlives can easily be tolerated. In fact, for extremely fast systems, equipment exists which mixes the components in the spray gun itself a fraction of a second before application.

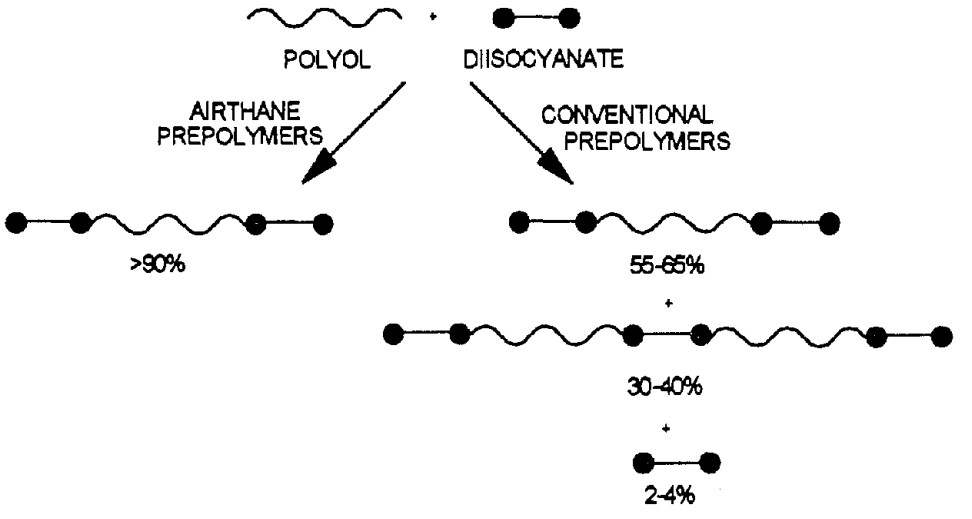
Perhaps more important for low VOC formulations, since short potlives can be tolerated, elevated temperatures can be used to lower the viscosity of the components instead of solvent. Using this approach, extremely high non-volatile material (NVM) coatings--approaching 100% NVM--may be possible using raw materials currently employed in conventional higher NVM formulations. Protective coating applicators and formulators are beginning to take advantage of these attributes to apply high quality primers and weatherable topcoats. This type of system works well in a controlled environment with stationery equipment, such as shop-applied rail car coatings or shop-coated structural steel. As equipment and formulations are refined, the potential also exists to take this type of equipment into the field.

This paper presents the use of newly developed isocyanate prepolymers--defined here as isocyanate/polyol adducts--as one alternative to formulating two component polyurethane topcoats. These prepolymers offer the advantages of a narrow molecular weight distribution, rapid viscosity reduction with increasing temperature or solvent level, very low diisocyanate monomer content, equivalent or improved film properties and weatherability characteristics compared to conventional coatings of this type, less sensitivity to catalyst level variability, and the ability to be formulated at a 1:1 volume ratio. While these prepolymers also are being used to formulate conventionally applied primers and topcoats[2], this paper will focus on the development of formulations specifically for plural component applied coatings where the unique characteristics of these prepolymers are used to overcome a number of formulating difficulties.

New Polyurethane Prepolymer Technology

Polyurethane prepolymers have been employed in certain segments of the coatings, adhesives, sealants, and elastomer industries for many years.[3] By forming a "pre"-polymer (see **Fig. 1**), diisocyanate monomer content is reduced and the reactivity of this partially reacted system is simpler to control. These prepolymers, however, have seen limited use in higher NVM coatings formulations. An examination of the synthesis process sheds some light on why this is so.

Figure 1: Comparison of Prepolymer Synthesis Technologies



The traditional synthesis process, depicted on the right side of Figure 1, typically involves the exothermic reaction of one equivalent of polyol with two equivalents of diisocyanate monomer. The desired end product, the isocyanate-capped polyol, makes up only around half of the weight of the final product mixture. Using this process, many of the diisocyanate monomer molecules react through both isocyanate groups, creating high molecular weight oligomers. These oligomeric species, which can be much larger than the simple 3:2 diisocyanate:polyol adduct shown in Figure 1, lead to the high solvent demand, relatively short pot lives, and poor sprayability of many prepolymer-based coatings formulations.

New technology, described in detail elsewhere,[4,5,6] has made available polyurethane prepolymers, tradenamed AIRTHANE® prepolymers, with half the viscosity of their conventional counterparts and extremely low diisocyanate monomer levels (<0.1% for aromatic isocyanates, <1.0% for aliphatic isocyanates). These materials, made by a process that keeps oligomer content very low, have the lower solvent demand and favorable pot life/dry time balance needed for high NVM formulating (see **Figures 2 and 3** and **Table 1**).

Figure 2: Comparison of Prepolymer Viscosities in Xylene

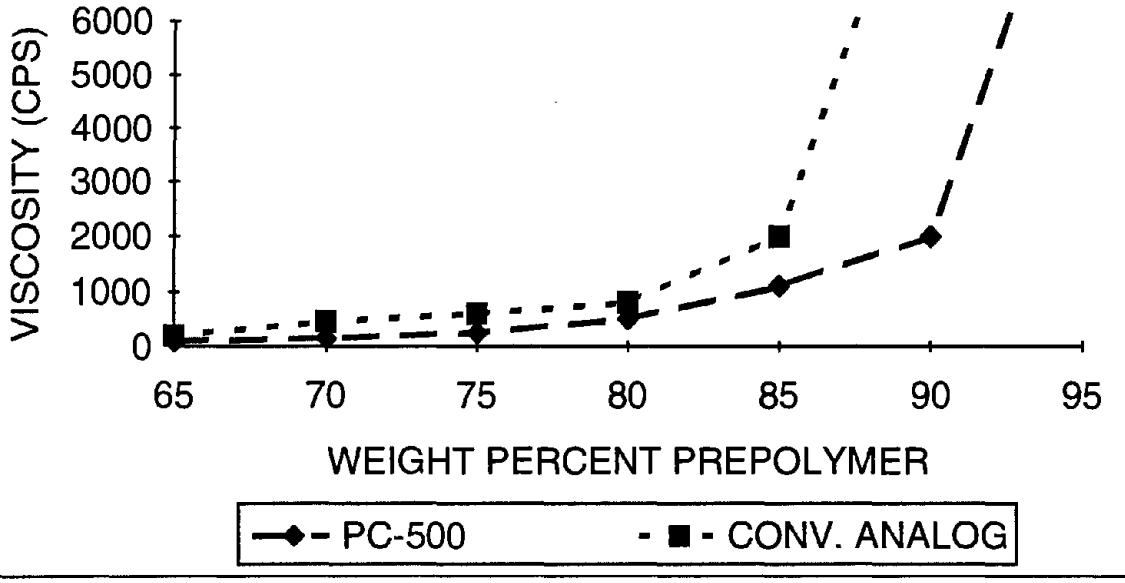


Figure 3: Comparison of Viscosity Build of Typical Prepolymer-based 2K Formulations

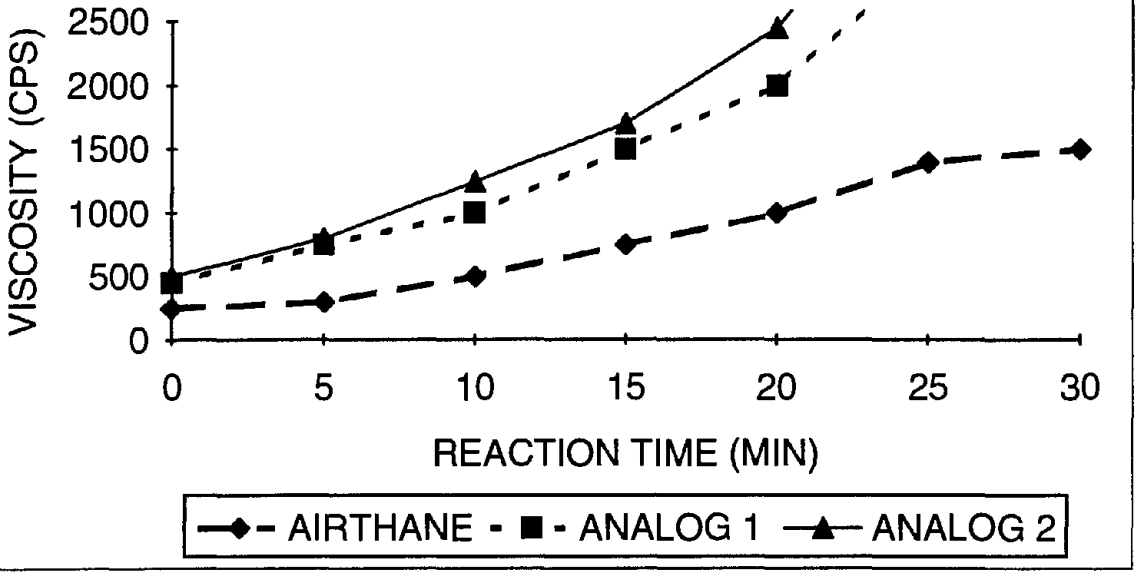


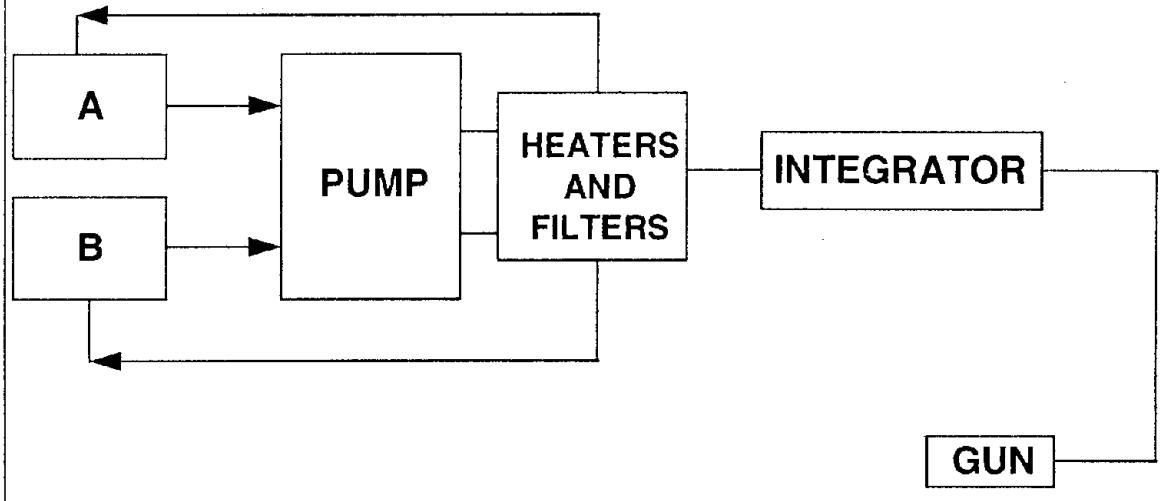
Table 1: Comparison of pot life (doubling of initial viscosity) and thin film cure times for a conventional prepolymer and its analog prepared by the Airthane prepolymer process.

Prepolymer	Wt. Solids (%)	Pot life	Cure time
Conventional Prepolymer	80	40 min	4.5 h
Airthane Prepolymer	85	2 h	6 h

Formulating for Plural Component Equipment

A typical plural component spray system contains the units described below in **Figure 4**. The reacting components are either pumped directly from their drums or from heated pots. The pumping mechanisms are typically reciprocating piston pumps that can deliver the two fluids at a set or variable volume ratio. The more common equipment will deliver a set ratio of 1:1, 2:1, or 4:1. Many set ups include in-line heaters and filters and may include a recirculation capability prior to the integrator. The integrator is a static mixer, often a proprietary design of the manufacturer. Following the integrator, the material is pumped through a "whip" section of hose to a standard airless or air-assisted airless spray gun.

Figure 4: Typical Plural Component Spray Equipment



The most critical event in the application of a successful system is the mixing of the components in the integrator. While different integrator designs affect how well the components mix, there are certain characteristics of the liquids that will lead to good mixing. It is generally believed[7] that in situations of laminar flow, it is easier to mix materials of more equal viscosity. If viscosities are unequal, it is easier to mix a small amount of a low viscosity material into a higher viscosity material than vice versa. Most plural component polyurethane formulations fall

into the latter catagory, where a relatively small low viscosity isocyanate component is mixed into a larger pigmented polyol component. However, it would be better yet if nearly equal amounts of materials with matching viscosities could be used.

Problems also arise when, as frequently happens, the delivered ratio of the proportioning equipment varies slightly from the nominal. While equipment technology is improving at a rapid rate, mechanical proportioners such as those described above can often vary by up to 5%. Equipment that is not very carefully maintained can vary even further. For consistent application of high quality coatings, the formulation needs to be somewhat forgiving of ratio variations. These fluctuations are much more detrimental to a high ratio formulation (4:1 and up) than to a 1:1 ratio formulation since changes in the volume of the small volume component will have a more significant effect on the stoichiometry of the reacting system. Our goal, then, in formulating two part polyurethane coatings for plural component application was to develop systems at a 1:1 volume mix ratio wherein in the two components would have similar viscosities at application temperature.

Formulation Details and Coating Performance

Two types of formulations were developed. The first, for more weatherable applications, is based on acrylic polyols and is considered a high NVM system. A typical formulation is detailed in **Table 2**. The isocyanate component of this formulation is a prepolymer based isophorone diisocyanate (IPDI) and a mixture of neopentyl glycol adipates. It has a nominal equivalent weight of 540 g/eq (on solids) and an average functionality of about 2.5. It is used in this formulation as an 85% NVM solution in methyl amyl ketone (MAK). This formulation is delivered at a 1:1 volume mix ratio with an NCO/OH of 1.1. The viscosity profiles versus temperature for the isocyanate and polyol components are shown in **Figures 5** and **6**, respectively. Note that the two components have very similar viscosities at the application temperature of 50°C.

Table 2: Typical formulation for high NVM weatherable topcoat.

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component I				
Chempol 17-3855	242.19	27.84	CCP	acrylic polyol
Zoldine RD4	21.53	2.84	Angus	reactive diluent
Ti-Pure R960	384.49	11.58	DuPont	pigment
Disperbyk 110	18.20	2.14	Byk-Chemie	dispersant
Dislon NS-30	1.58	0.21	King Industries	thixotrope
Tinuvin 292	8.87	1.06	Ciba-Geigy	HALS
Tinuvin 400	10.44	1.26	Ciba-Geigy	UVA
Tego 980	4.14	0.52	Tego Chemie	air release
DABCO 120	0.59	0.07	Air Products	catalyst
18% Zn-Oct	3.52	0.40	OMG	catalyst
MAK	13.96	2.05		solvent
Subtotal	709.51	**49.97**		

Table 2: (continued)

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component II				
Airthane ASN-540M	442.64	**50.03**	Air Products	isocyanate prepolymer
Totals	1152.15	**100.00**		

Weight percent NVM = 87.76%; Volume percent NVM = 79.94%; PVC = 15.27%; VOC = 1.41 lb/gal (169 g/L); Mix Ratio: 1:1

Figure 5: Thermal Profile for ASN-540M

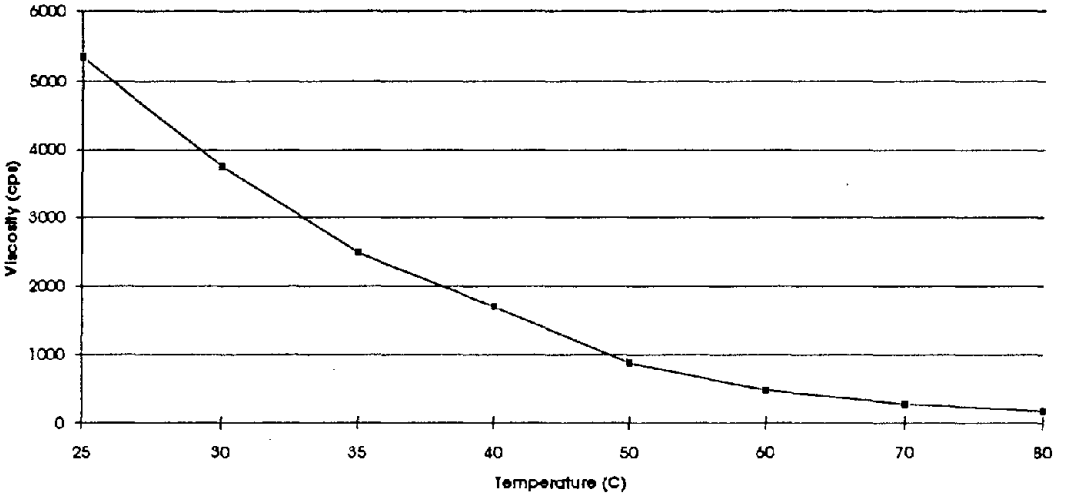
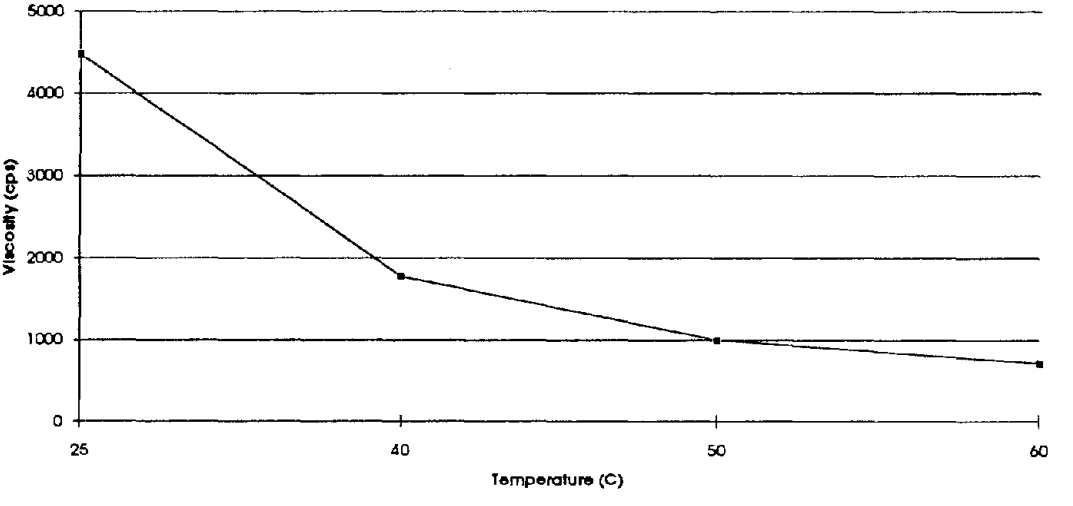


Figure 6: Thermal Profile for Pigment Grind of High NVM Formulation



The second type of formulation developed is based on polyester polyols and can be formulated at less than 0.20 lb/gal (24 g/L). A typical formulation is detailed in **Table 3**. The isocyanate component of this formulation is a mixture of the prepolymer used above with polyisocyanates based on hexamethylene diisocyanate (HDI). This unique combination of isocyanates provides low viscosity, high crosslink density, and sufficient molecular weight to formulate at a 1:1 mix ratio with an NCO/OH of 1.1. The use of the low oligomer prepolymer is critical to the success of this mixture. A conventional prepolymer would have too high a viscosity and most likely impart poor sprayability to the formulation. The viscosity profiles versus temperature for the isocyanate and polyol components are shown in **Figures 7** and **8**, respectively. Note, again, that the two components have very similar viscosities at the application temperature of 50°C.

Table 3: Typical formulation for very low VOC topcoat.

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component I				
Chempol 18-2244	192.10	20.11	CCP	polyester polyol
Tone 0301	82.33	9.10	Union Carbide	poly-caprolactone
Ti-Pure R960	483.85	14.57	DuPont	pigment
Disperbyk 110	21.47	2.52	Byk-Chemie	dispersant
Dislon NS-30	1.99	0.27	King Industries	thixotrope
Tinuvin 292	7.44	0.89	Ciba-Geigy	HALS
Tinuvin 400	8.76	1.06	Ciba-Geigy	UVA
Tego 980	3.72	0.47	Tego Chemie	air release
Byk 320	4.29	0.61	Byk-Chemie	flow aid
DABCO 120	0.37	0.04	Air Products	catalyst
18% Zn-Oct	4.43	0.51	OMG	catalyst
Subtotal	810.75	**50.15**		
Component II				
Airthane ASN-540M	234.98	25.38	Air Products	isocyanate prepolymer
Desmodur N3300	117.49	12.12	Miles/Bayer	HDI isocyanurate
Luxate HD-100	117.49	12.35	Olin	HDI uretdione
Subtotal	469.96	**49.85**		
Totals	1280.71	**100.00**		

Weight percent NVM = 98.74%; Volume percent NVM = 97.94%; PVC = 15.57%; VOC = 0.16 lb/gal (19 g/L); Mix Ratio: 1:1

Figure 7: Thermal Profile for 100% NVM Isocyanate Blend

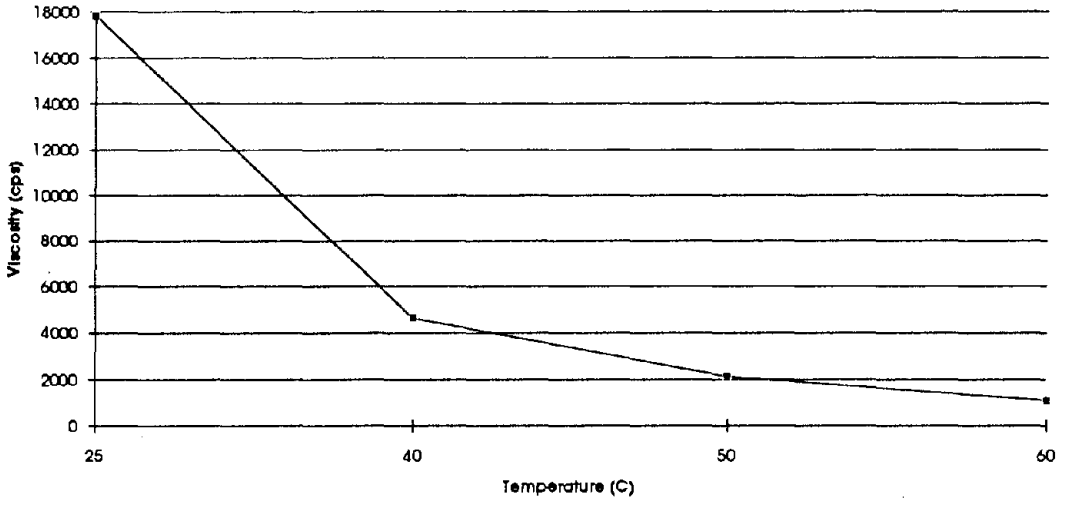
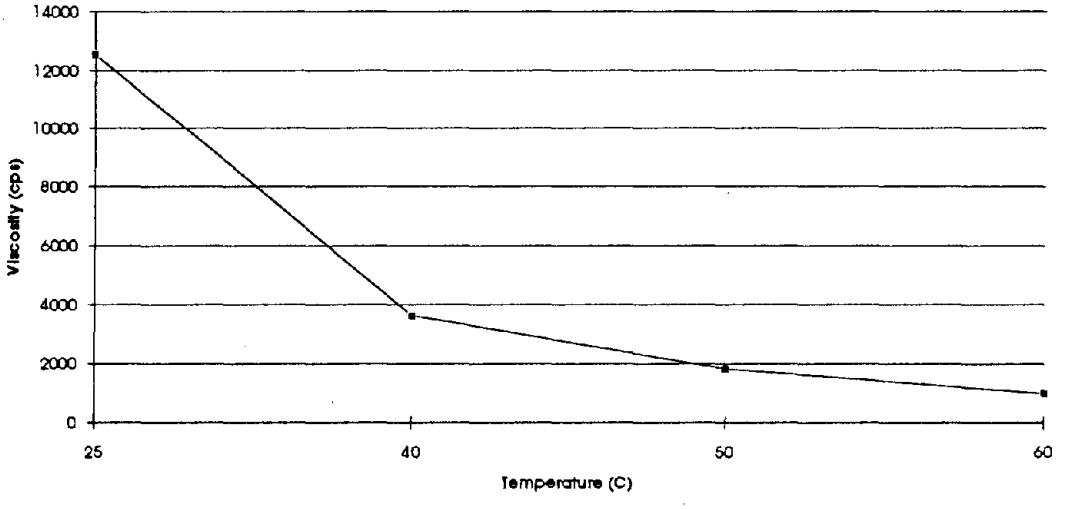


Figure 8: Thermal Profile for Very Low VOC Pigment Grind



The properties of these coatings are representative of traditional solvent borne urethanes and compare well with those of an HDI isocyanurate control. Physical and mechanical property comparisons are shown in **Table 4.** It is important to note that handling the isocyanurate control was much more difficult than the prepolymer based formulations. The control formulation required a 4:1 mix ratio (non-integer mix ratios were needed with other control formulations tried) and showed an extreme sensitivity to catalyst level. This was demonstrated by measuring the pot life of each of the formulations. The prepolymer formulations described above did not gel for several hours when mixed at ambient temperatures. The control formulations with no catalyst also had a pot life of several hours. The control formulations with the same modest catalyst levels used with the prepolymers, however, gelled in less than 15 minutes. Current work

is aimed at better quantifying the relative catalysis lattitude of the prepolymer and control formulations, but it is apparent that the prepolymer approach is much less sensitive to variations in catalyst level.

Table 4: Representative Coating Film Property Comparison

Property	Prepolymer Acrylic	Isocyanurate Acrylic Control	Prepolymer Polyester
Set time (hours)	3	3	2
Dry hard (hours)	16	15.5	3
Pencil Hardness	HB	HB	HB
Dry Adhesion (ASTM D3359)	5A	4A	4A
Wet Adhesion (24 h, D3359)	4A	4A	4A
Impact (D/R in-lb)	160/160	160/160	160/160
MEK rubs	100+	100+	100+
60° Gloss	92.6	94.7	95.3
Gloss Retention (1000 h, UV-B313)	92%	88%	97%

Plural Component Application

Application trials of the two sample formulations were conducted at Graco, Inc. Engineering Labs in Franklin Park, IL. The pump used was a Graco Bulldog 206-740 fixed at a 1:1 volume mix ratio with a 32:1 air/fluid pump ratio. This set-up utilizes equivalent volume dual pistons which fill on the up-stroke and empty on the down stroke. The reacting materials were pumped directly from 5 gallon pails, through in-line heaters and 60 mesh filters, and could be recirculated through this cycle to heat the material fully. The fluid lines to the mixing manifold were resistively heated. The mixing element was a 3/8" diameter static mixer with 30 elements. Both formulations were easily pumped at temperatures from 120°F to 150°F. The appearance and properties of the applied material also indicated excellent mixing of the reactive components. Applied films were smooth and uniform, and coating film performance was as expected. The coatings were applied by airless (517, 617, and 619 tips) and high pressure air-assisted airless (608 cap, 100 psi atomizing pressure) methods. Applications characteristics were fair. The near-zero VOC, polyester-based formulation atomized better than the higher solids acrylic formulation; however, both formulations showed some tailing. Larger tips and slightly higher application temperatures may have improved the spray pattern, but the trial was limited in the amount of available formulated paint at this writing.

CONCLUSIONS

The development of low oligomer content isocyanate terminated prepolymers (diisocyanate/polyol adducts) has introduced a new option in formulating very high NVM two component urethane coatings. The low solvent demand of these prepolymers and their rapid viscosity decrease with increasing temperature has allowed the use of this type of material for

the first time in high performance, plural component applied coatings. The higher equivalent weight of these prepolymers allows the formulator to develop paints at a 1:1 volume mix ratio. These formulations showed good handling and excellent mixing properties. Coatings applied by airless and air-assisted airless methods showed fair atomization and excellent flow out. The performance of these coatings is as good as, or better than, high mix ratio polyisocyanate-based control formulations.

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7. See, for example: Tadmor and Gogos, Principles of Polymer Processing, Wiley, 1979; Middleman, Fundamentals of Polymer Processing, McGraw Hill, 1977; and Oldshue, Fluid Mixing Technology, McGraw Hill, 1983.

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SESSION 9

LOW- AND NO-VOC COATINGS-PART 1

PAPERS PRESENTED:

"Organsosilanes in Low VOC Coatings"
by
Kamlesh Panjnani
University of Southern Mississippi
Hattiesburg, Mississippi

"Polyester Oligomers of Narrowed Molecular Weight Distribution"
by
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"New Epoxy/Anhydride Chemistry for Durable, High Solids Coatings"
by
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ORGANSOSILANES IN LOW VOC COATINGS

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INTRODUCTION

The genus, *Lesquerella*, is a new domestic crop with potential industrial significance, and is native to the Southwest United States. Three hydroxy fatty acids (Figure 1), lesquerolic, densipolic, and auricolic acids, are the primary fatty acids in lesquerella oil (LO) and make up approximately 60% of the oil composition.[1-7] Lesquerella is particularly attractive as a raw material since, unlike other domestic vegetable oils, the three major fatty acids in lesquerella are structurally similar to ricinoleic acid (Figure 1), the principal fatty acid of castor oil (CO). Currently, CO and its derivatives are the sole commercial source of hydroxyl fatty acid.[8-9] However, since the early 1970's, all CO consumed by the United States has been imported. Price instability and inconsistent supply have handicapped end-users, making corporate planning difficult. Consequently, a domestic, economically-attractive, and high performance CO substitute is desirable. However, lesquerella is a semi-drying oil with an iodine value of 102-116, and therefore, must be modified if used in air dry coatings.[10-13]

Silicon-containing polymers have widely been used in industry to improve flow, leveling, exterior durability, electrical resistance, corrosion resistance, and weather resistance. Structurally, most silicon-containing materials have one or more Si-O bonds and are therefore classified as silicones. Organosilane polymers, on the other hand, contain a hydrolytically stable Si-C bond which confers property enhancements normally associated with silicone modification, i.e., increased thermal stability, improved solubility, enhanced processibility, and better weatherability.[14-16] Thames, et al reported the synthesis, characterization, and evaluation of powder coatings containing organosilane diacids and anhydrides as crosslinking agents. These coatings display improved gloss, gloss retention, flow, and leveling.[17-19] Furthermore, Thames, et al have confirmed that silane incorporation lowers glass transition temperatures, enhances thermal stability, and improves solubility in organic solvents.[20-21] Thus, this investigation focused on the combined influence of pendent organosilane dicarboxylic acids in LO based coatings.

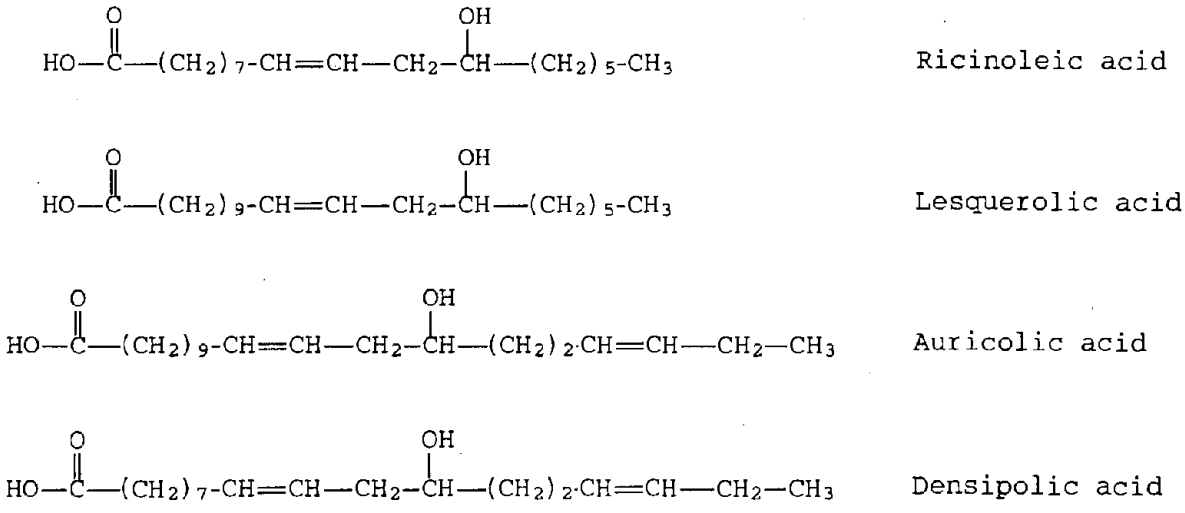


Figure 1

EXPERIMENTAL

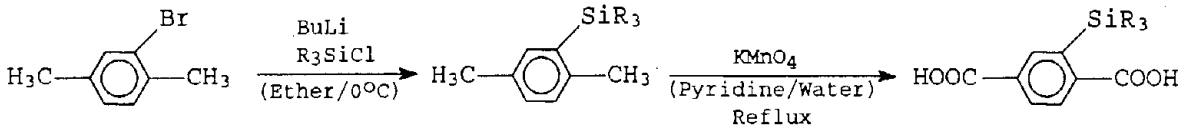
Materials

Lesquerella oil (refined from *Lesquerella fendleri*) was purchased from International Flora Technology Ltd. Phthalic anhydride, terephthalic acid, and trimethylol ethane were obtained from Aldrich Chemical Company, Inc. Lithium ricinoleate was purchased from Pfaltz & Bauer, Inc. Cobalt, zirconium, and manganese driers were provided by Nuodex, Inc. as 6% metal solutions. Exkin No. 2, an antiskinning agent (methyl ethyl ketoxime), was obtained from Huls America, Inc. Activ 8, a drier accelerator, and Nacure 155 (dinonyl naphthalene disulfonic acid) were provided by R. T. Vanderbilt Co., Inc. and King Industries, respectively. Cargill 23-2317, a highly methylated melamine resin, was supplied by Cargill, Inc. All additives, solvents, catalyst, and raw materials with the exception of the organosilane dicarboxylic acids were used as received.

The monosubstituted pendent organosilane dicarboxylic acids, 2-trimethylsilyl terephthalic acid, 2-dimethylphenylsilyl terephthalic acid, 2-diphenylmethylsilyl terephthalic acid, and 2-triphenylsilyl terephthalic acid, were synthesized according to Scheme 1. The disubstituted pendent organosilane dicarboxylic acids, 2,5-di(trimethylsilyl) terephthalic acid and 2,5-di(dimethylphenylsilyl) terephthalic acid, were synthesized according to Scheme 2.

Synthesis of Monosubstituted Organosilane Dicarboxylic Acids - Scheme 1

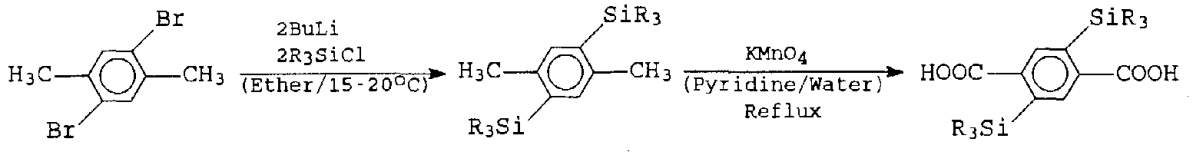
n-Butyl lithium (10 M) in hexanes (10% molar excess) was added to a solution of 2-bromo-*p*-xylene in anhydrous ether at 0°C under nitrogen. After one hour, the desired chlorosilane (10% molar excess) was added dropwise, lithium chloride was subsequently removed by filtration, and the solvents were removed *in vacuo*. The intermediates formed were purified by vacuum distillation or recrystallization followed by oxidation with $KMnO_4$ in a water/pyridine mixture to give the respective monosubstituted organosilane dicarboxylic acids. All monosubstituted organosilane intermediates and dicarboxylic acids were characterized via Fourier transform infra red (FTIR), nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis.



Scheme 1

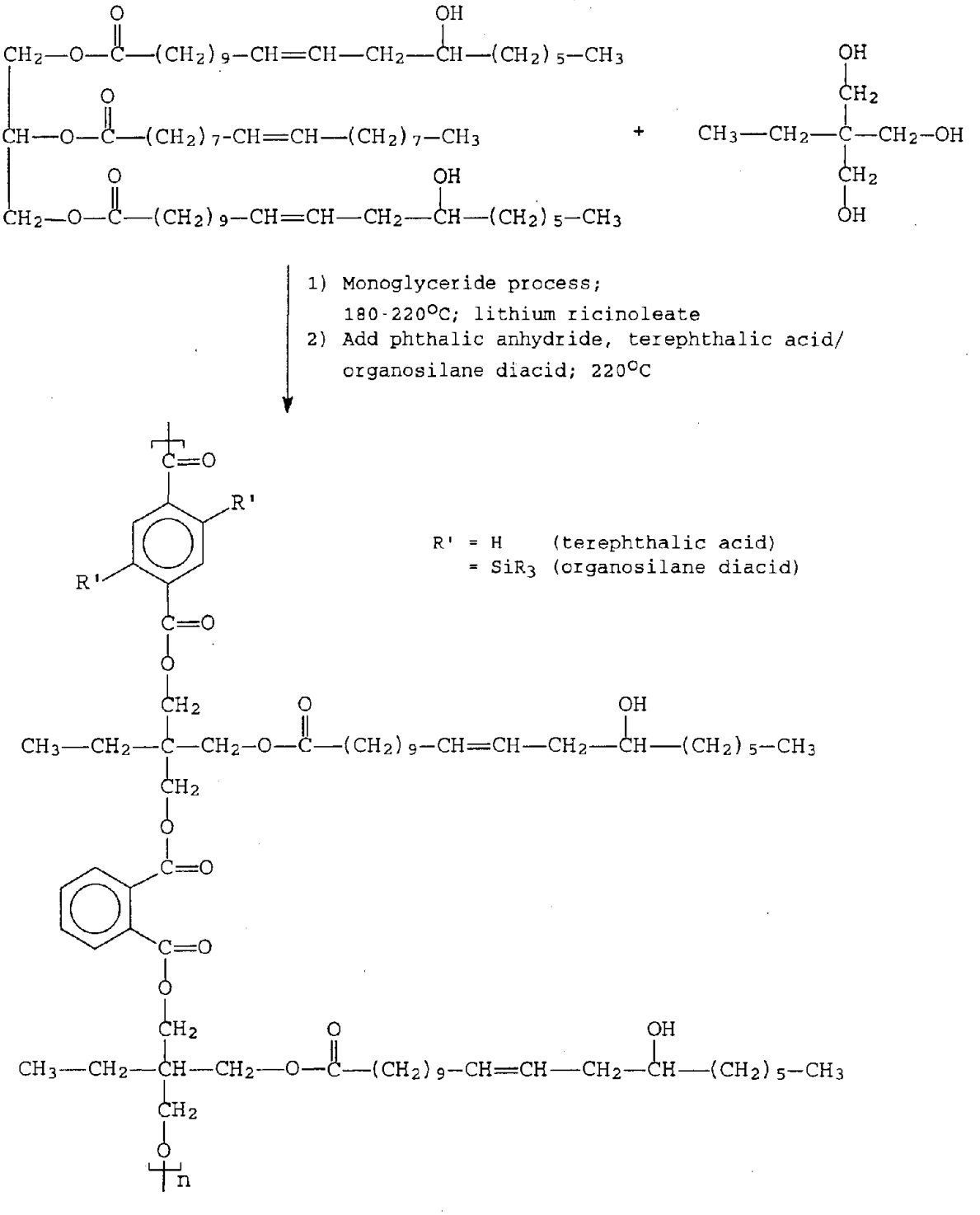
Synthesis of Disubstituted Organosilane Dicarboxylic Acids - Scheme 2

n-Butyl lithium (10 M) in hexanes (10% molar excess) was added to a solution of 2,5-dibromo-*p*-xylene in anhydrous ether at 15-20°C under nitrogen. After one hour, the desired chlorosilane (10% molar excess) was added dropwise. The process of metalation and addition of chlorosilane was completed again in order to obtain the disubstituted product. The intermediates formed were purified by recrystallization and subsequently oxidized with $KMnO_4$ in a water/pyridine mixture to the respective disubstituted organosilane dicarboxylic acids. All disubstituted organosilane intermediates and dicarboxylic acids were characterized via FTIR, NMR spectroscopy, and elemental analysis.



Scheme 2

Alkyd Resin Synthesis - Scheme 3



Scheme 3

Medium oil length polyester resins (55% oil length), were synthesized via the monoglyceride process.[22] The control formulation was synthesized with LO, trimethylol ethane, phthalic anhydride, and terephthalic acid. In the experimental formulations, terephthalic acid was replaced with organosilane dicarboxylic acid. All alkyd resins were synthesized at an alkyd constant of 1.04 and 10% excess hydroxyl. The polyesterification reaction was monitored by titrating the reaction mixture with alcoholic potassium hydroxide (KOH) and terminated at an acid value of 8±2 mg KOH/g of sample. The percent non-volatiles of each alkyd was determined from the weight loss on heating samples at 150°C until constant weight was attained (ASTM D-1644).

Air Drying Coating Formulation

A control and six experimental air drying coatings were formulated by adding cobalt, manganese, and zirconium driers, Activ 8, and Exkin No. 2, to each of the polyester resins. All formulation components (Table 1) were mixed with a high speed stirrer at 500 rpm for 15 minutes, and allowed to stabilize for 24 hours prior to application. With a draw-down bar, 4 mils thick coatings were applied onto a 3" x 6" x 0.2" low-carbon, mild steel, QD-36 untreated panels previously wiped with methyl ethyl ketone (MEK). The films were air dried for one week before testing.

Table 1 - Air Drying Coating Formulation

Ingredient	% by Weight
Polyester (80% non-volatiles)	92.50
Cobalt drier (6% metal)	1.10
Manganese drier (6% metal)	0.70
Zirconium drier (6% metal)	1.90
Activ 8	1.90
Exkin No. 2	1.90
Total	100.00

Alkyd-Melamine Coating Formulation

The control and six experimental polyester resins were crosslinked with Cargill 23-2317. All coatings were formulated at 70:30 alkyd-melamine ratio by weight. Nacure 155 was added to catayze the crosslinking reaction. All the components in the formulation (Table 2) were mixed with a high speed stirrer at 500 rpm for 15 minutes and then allowed to stabilize for 24 hours prior to coating application. With a draw-down bar, 4 mils thick coatings were applied onto a 3" x 6" x 0.2" low-carbon, mild

steel, QD-36 untreated panels previously wiped with MEK. The films were heat cured at 120°C for 30 minutes. The cured films were equilibrated for seven days before testing.

Table 2 - Thermosetting Alkyd-Melamine Coating Formulation

Ingredient	% by Weight
Polyester (80% non volatiles)	68.70
Cargill 23-2317 (84% non volatiles)	28.00
Nacure 155	3.30
Total	100.00
Alkyd:Melamine ratio (by weight)	70:30

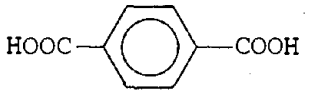
Testing Equipment

Polyester molecular weights were determined with a Perkin Elmer model 250 binary LC pump, equipped with model 13 ultra-violet detector. Three gel permeation chromatography (GPC) columns of pore size 50, 500, and 10^4 angstroms were placed in series and calibrated using polystyrene standards. The GPC results were analyzed with GPC data analysis software from Polymer Labs (PL Caliber version 5.11). Polyester viscosity was measured at 80% solids in xylene, on a Brookfield viscometer model DV-II (ASTM D-2196).

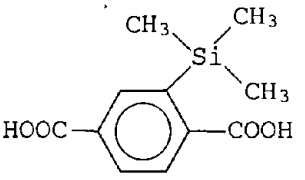
Dry film thicknesses were measured by a Gardco Minitest 4000 Microprocessor coating thickness gauge (ASTM D-1186). Impact resistance was determined with a BYK Gardner impact tester model IG-1120, using a 1.82 Kg., 1.27 cm. diameter steel pin (ASTM D-2794). Pencil hardness was expressed in terms of pencil leads of known hardness (ASTM D-3363). Adhesion was assessed by applying and removing a pressure-sensitive tape over a crosshatch constructed by eleven cutting blades (ASTM D-3359). Flexibility was measured by bending coated panels on a Paul N. Gardner, Model MN-CM conical mandrel (ASTM D-522).

RESULTS AND DISCUSSION

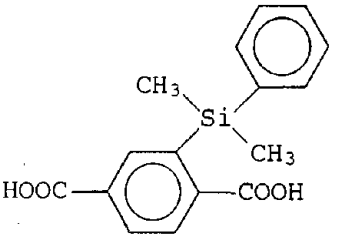
Gel permeation chromatography data (Table 3), indicate that the molecular weight of the polyesters ranged from 3500-4100 g/mol based on polystyrene standards. However, the acid values for all fell in the 8±2 range thus approximating a molecular weight of 5500-6500 g/mol.[23]



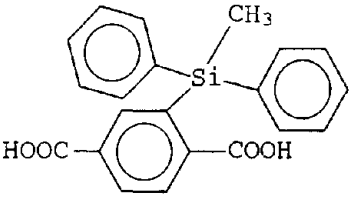
Terephthalic acid
(Control)



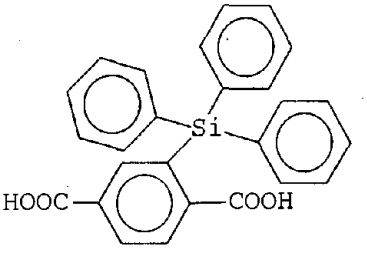
2-Trimethylsilyl
terephthalic acid
(Formulation #2)



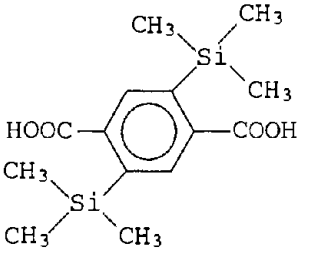
2-Dimethylphenylsilyl
terephthalic acid
(Formulation #3)



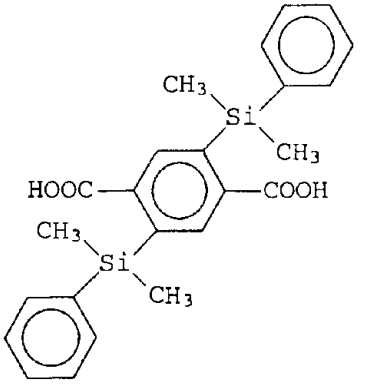
2-Diphenylmethylsilyl
terephthalic acid
(Formulation #4)



2-Triphenylsilyl
terephthalic acid
(Formulation #5)



2,5-Di(trimethylsilyl)
terephthalic acid
(Formulation #6)



2,5-Di(dimethylphenylsilyl)
terephthalic acid
(Formulation #7)

Figure 2

Viscosity and appearance measurements are listed in Table 3. The control, and formulations 2, 3, and 6 were cloudy. On the other hand, formulations 4, 5, and 7 were clear and lower in viscosity. The clarity and reduced viscosity is attributable to the high reactivity and increased acidity of carboxyl in 2-diphenylmethylsilyl terephthalic acid, 2-triphenylsilyl

terephthalic acid, and 2,5-di(dimethylphenylsilyl) terephthalic acid as a result of (p-d) π bonding.[19] The increased reactivity reduces synthesis time, therefore limiting viscosity increases due to thermal polymerization. The enhanced acidity of the carboxyl group and the existence of silane moieties bestows improved solubility in organic media and thus a clear polyester. The structure and designation of the dicarboxylic acids used in the polyester syntheses are included in Figure 2.

Table 3 - Polyester Properties

Formulation	Appearance	Viscosity (cps)	Molecular Weight (M_n)	Acid Number mg KOH/g
Control	Cloudy	1750	3589	9.6
Formulation #2	Cloudy	1840	4006	8.5
Formulation #3	Cloudy	2290	3556	9.4
Formulation #4	Clear	1140	4079	9.2
Formulation #5	Clear	830	3812	9.5
Formulation #6	Cloudy	1690	3876	9.4
Formulation #7	Clear	1040	3913	9.2

The physical properties of the air drying coating formulations are included in Table 4. All coating formulations showed excellent impact resistance, flexibility, and adhesion. However, the control formulation was tacky even after one week dry time, indicating incomplete curing via oxidative polymerization. Pencil hardness data corroborated incomplete curing of the control polyester. Dry times for the experimental polymers decreased with increasing aromatic content of organosilane diacids.

Table 4 - Air Drying Coating Properties

Formulation	Drying Time (hr)	Pencil Hardness	Impact Resistance (inch-lbs)	Flexibility (inch)	Adhesion
Control	>168	<6B	160+/160+	0.125	5B
Formulation #2	72	HB	160+/160+	0.125	5B
Formulation #3	24	HB	160+/160+	0.125	5B
Formulation #4	16	HB	160+/160+	0.125	5B
Formulation #5	24	HB	160+/160+	0.125	5B
Formulation #6	48	HB	160+/160+	0.125	5B
Formulation #7	16	HB	160+/160+	0.125	5B

The thermosetting polyester-melamine crosslinked film properties are listed in Table 5. All formulations gave excellent flexibility, impact resistance, and adhesion. Crosslink density (MEK rub resistance) and pencil hardness of the experimental formulations were better than the control, and improved with increasing aromatic content in the silane diacids; a feature of increased (p-d) π bonding.

Table 5 - Polyester-Melamine Coating Properties

Formulation	Pencil Hardness	Impact Resistance (inch-lbs)	Flexibility (inch)	Adhesion	MEK Rubs
Control	2H	160+/160+	0.125	5B	25
Formulation #2	2H	160+/160+	0.125	5B	25
Formulation #3	4H	160+/160+	0.125	5B	40
Formulation #4	4H	160+/160+	0.125	5B	60
Formulation #5	4H	160+/160+	0.125	5B	75
Formulation #6	2H	160+/160+	0.125	5B	35
Formulation #7	4H	160+/160+	0.125	5B	65

CONCLUSIONS

The use of organosilane dicarboxylic acids in LO based polyesters provided a polyester of lower viscosity than a corresponding, non-silane modified control polymer synthesized and formulated to the same molecular weight and non-volatiles, respectively. In air drying formulations, the organosilane modified coatings dried faster to harder films. Furthermore, organosilane, thermosetting polyester-melamine polymers exhibited improved pencil hardness and MEK resistance, properties accruing from high crosslink density. The improvements were obtained without losses in adhesion, flexibility, or impact resistance.

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POLYESTER OLIGOMERS OF NARROWED MOLECULAR WEIGHT DISTRIBUTION

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ABSTRACT

Attempts to reduce the VOCs in thermosetting solvent borne enamels have led to the use of very low molecular weight polyester oligomers. Unfortunately, traditional polyester preparation techniques leave relatively large amounts of unreacted polyols or polyacids that contribute to VOC, and still produce molecular weight fractions larger than desired. This leads to diminishing returns in VOC reductions. A technique is described to narrow this molecular weight distribution and eliminate low molecular weight residual reactants by a series of alternating stepwise reactions using oxirane and anhydride reactants. The oligomers produced are described and characterized, and their performance in high solids baking enamels reviewed. Difficulties in pigmentation stability in regard to acid catalyst adsorption, gloss and film performance are described as well as corrective techniques for use with these oligomers.

Lack of high molecular weight fractions and possible ionic content from catalyst-polymer bonding cause problems in obtaining high resistivity. Synthetic approaches giving higher aliphatic content in the polyesters which counter this and lead to high resistivity paints are described.

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BACKGROUND

Polyester oligomers crosslinked with hexamethoxymethyl-melamine(HMMM) type resins have become increasingly popular as a high solids answer to regulatory demands for lowered volatile organic compound (VOC) coatings. They offer economical baking enamels of low VOCs with an excellent combination of hardness, flexibility and resistance properties. The formula below illustrates such a simple white high gloss baking enamel for spray application.

ILLUSTRATION I

White High Gloss Spray Enamel
Polyester A

Lb.	Gal.	Material
430.80	13.06	Rutile Titanium Dioxide
172.32	19.02	90% Isophthalic Polyester A
21.54	3.19	n-Butanol
64.62	8.91	Xylene
6.46	0.89	Viscosity Suspension and Sag Control Additive
695.74	45.07	

Disperse to 7+ N.S.

278.58	30.75	90% Isophthalic Polyester A
161.55	16.16	Hexamehoxymethyl melamine
4.06	0.51	p-TSA (40% solution)
0.72	0.09	Anti-Crater Additive
53.85	7.43	Xylene
1194.50	100.01	

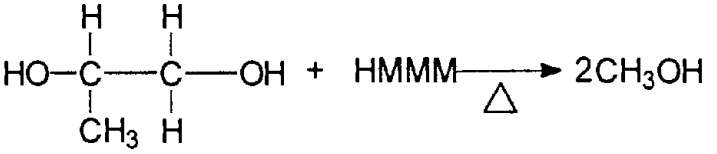
ANALYSIS:

Pigment/Binder Ratio	0.8/1.0
Percent Solids, Weight	81.4
Percent Solids, Volume	69.2
Viscosity at 25°C (approx. Seconds, #4 Ford Cup)	50
Theoretical VOC:	
Pounds/Gallon	1.85
Grams/Liter	222
Determined VOC, via ASTM Method D3960	
Pounds/Gallon	2.57
Grams/Liter	308
Typical Baking Schedule, Min/°F	15-20/300-350

More recently there has been pressure for further VOC reductions; for example, the 2.3 lb/gal or 275 g/l requirements in California. As the above formula illustrates, there is not really a lot (15% by weight) of solvent left which can be removed from these paints. This is especially significant when one considers that a substantial portion of the VOC is alcohols (methanol) evolved from the crosslinking resin, and some low molecular weight esters. This is illustrated by a comparison of the theoretical VOC (solvent evolved) with the determined VOC as measured by ASTM 3960. These crosslinker-derived emissions would represent about 28% of the total from the paint.

To achieve the solvent reduction needed to meet the newer VOC guidelines, one sees one has to remove approximately all of the solvent from the Polyester Oligomer A of the above paint example. This corresponds to approximately an 85% NV white paint as per the above formula. If one further reduces the molecular weight (MW) of the polyester oligomer in an attempt to maintain the same viscosity at the reduced solvent level, the determined NV of the polyester does not rise much above the original 90%. This is due to increased amounts of unreacted and volatile glycols and simple esters. Those function at best as weak solvents. Even anticipating that these would not volatilize from the film because of reaction with the hexamethoxy-methylmelamine (HMMM) resins, they still lead to diminishing returns in terms of emissions. One must consider the reaction of propylene or neopentyl glycol with HMMM and the attendant methanol evolution.

ILLUSTRATION II



(76 MW) Volatile ⟶ (64 MW) Volatile

Actually, the diminishing VOC returns seen on molecular weight reduction of these oligomers has been long recognized as per the 1981 Journal of Coatings Technology article by Belote and Blount.[1]

As they discussed in their study of a series of neopentyl-adipic-phthalic polyesters of varying molecular weights, little VOC reduction was obtained in going below 1000 MW, as is roughly illustrated below:

TABLE I

Mn	Theoretical VOC	Determined VOC @ 325°F	Determined VOC @ 250°F
1400	3.2	3.5	3.2
1200	2.6	3.0	2.8
1000	2.5	2.9	2.7
800	2.4	2.9	2.7
600	2.2	2.9	2.7

Generally this type of phenomenon is noted with the wide variety of polyester oligomers used in these coatings.

CONSIDERATION OF THE MOLECULAR WEIGHT DISTRIBUTION

Since the molecular weight of these oligomers is low and little is gained by any further molecular weight reduction, one is led to consider viscosity improvements by manipulation of the molecular weight distribution. A technique for doing this is discussed below.

NARROWED MOLECULAR WEIGHT DISTRIBUTION TECHNIQUES

The use of certain polyols such as 2,2,4-trimethyl-1,3-pentanediol, having hydroxyl functionalities of unequal reactivity, can provide self limiting polyester chain growth if carefully balanced with other polyols.

ALTERNATING STEPWISE REACTION APPROACH

A recognized approach to controlling the molecular weight distribution of such polyester oligomers is to prepare them in a stepwise fashion at temperatures below those resulting in transesterification reactions which could broaden the distribution. Ordinarily, one would not do this in polyesterification reactions due to the time involved in the many steps. The low molecular weights desired in the oligomers, however, makes the approach feasible. One would employ a reactant in each step capable of rapidly reacting to completion at lower temperatures. Thus, one would alternate the different reactants in each subsequent step such that the new reactant is only reactive with the resultant functionality derived in the prior step, but not with functionality derived from its own reaction. Thus it theoretically becomes possible to force the reaction of every initial molecule one time. This is done by balancing the number of moles of reactant with the equivalents of reactive functionality on the molecule derived in the prior step and carrying the reaction to completion. The alternation of steps insures that all the molecules are increased in size only by the increment derived from the reactant and thus remain theoretically identical.

Fortunately, two common reaction types offer possibilities for carrying out this approach. These are the half ester reaction of an anhydride with hydroxyl yielding a carboxyl group, and the oxirane reaction with carboxyls liberating a hydroxyl. Both can be carried out at 120°C in one to four hours depending on catalysts chosen.

Since it is desired to build oligomers with functionalities of two or greater, the reaction would be initiated with a multifunctional molecule. The reaction sequence could thus be seen in Illustration III with suitable abbreviations.

ILLUSTRATION III

		M.W.
Initiator	HO-R-OH	76
+2 Anhydrides (Anh)	HOOC - Anh-R-Anh - COOH	372
+2 Oxiranes (Ox)	HO - Ox-Anh-R-Anh-Ox - OH	488
+2 Anhydries	HOOC - Anh-Ox-Anh-R-Anh-Ox-Anh - COOH	784
+2 Oxiranes	HO - Ox-Anh-Ox-Anh-R-Anh Ox-Anh-Ox - OH	900

Since the number of steps is relatively small to build oligomers of the molecular weight desired for these low VOC coatings, and the time of each step relatively short, the economics is not disturbed by lengthy reaction times. The reaction sequence described above would entail about twelve hours, comparable to conventional polyesterification reaction times.

The immediate question is, whether such a scheme can indeed give oligomers free of side reactions and of very narrow molecular weight distribution. To investigate this, we prepared an oligomer from succinic anhydride and cyclohexene oxide (CHOx) using an adipic acid initiator in five steps (Illustration IV). The results are listed in Tables II and III.

ILLUSTRATION IV

Step 1: 2 moles of cyclohexane oxide (CHOx) reacted with 1 mole of adipic acid (AdA), yielding

HO-CHOx-AdA-CHOx-OH (342 MW)

Step 2: 2 moles of succinic anhydride (SU) added yielding

HOOC-SU-CHOx-AdA-CHOx-SU-COOH (542 MW)

Step 3: 2 moles of cyclohexane oxide added, yielding

HO-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-OH (738 MW)

Step 4: 2 moles of succinic anhydride added, yielding

HOOC-SU-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-SU-COOH (938 MW)

Step 5 2 moles of cyclohexane oxide, yielding

HO-CHOx-SU-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-SU-CHO-OH (1134 MW)

TABLE II

GPC Results

Cyclohexane Oxide-Succinic Anhydride Oligomerization (Against Polystyrene Standards)

Step	Theo. Mn	Mn	Mw	Pd
1	342	325	344	1.06
2	542	500	554	1.11
3	738	691	803	1.16
4	938	845	943	1.12
5	1134	1067	1175	1.10
Conventional	1134	1163	2445	2.10

Indeed, the results indicate very narrow molecular weight distributions are possible.

TABLE III

90% Oligomer in Ethoxyethyl Propionate

	Oxirane Anhydride	Random Polyesterification
Step 1 (342 MW)	26 Stokes	---
Step 3 (738 MW)	649 Stokes	---
Step 5 (1134 MW)	7300 Stokes	---
80% Solution	49 Stokes	>150 Stokes

USE OF THE TECHNIQUE

Fortunately, there are a good number of economical oxiranes and anhydrides which can be used to custom design a wide variety of oligomers of different molecular weights and compositions. Oligomer compositions can be prepared while varying the potential film hardness from aromatic content, potential flexibility from aliphatic content, reactivity from end group functionality (hydroxyl-carboxyl), etc. While higher molecular weight materials can be prepared, those most suitable for coatings VOC reduction generally consist of three to five steps.

When different anhydrides or oxiranes are used in preparing oligomers, they can be used in separated steps to keep molecular uniformity. Thus, different reactants can be kept at the same position on the oligomer chains, and in the same molar ratio in each chain. For convenience, they may also be mixed in the same step, which can yield several similar species differing in composition but relatively close in molecular weight and average viscosity. For example, one might use an equimolar mixture of phthalic and succinic anhydrides in the second step of a three step procedure.

PROPYLENE PHTHALATE ADIPATE OLIGOMERS

The GPC data below represents an economical propylene phthalate adipate oligomer synthesized by a similar route. It is an oligomer with a molar ratio of 4 polyols to 3 poly acids.

A polyester oligomer of essentially the same molar composition was prepared in a simple, one-step polyesterification process by replacing the propylene oxide with propylene glycol. Water was removed via a packed-column condenser at 410°F. Viscosity, nonvolatile and GPC comparisons were run on the two oligomers (Table IV).

TABLE IV

	Propylene Oxide 3-Step Oligomer	One-Step Oligomer
Nonvolatile	94%	92%
95% Viscosity in EEP	227	404
GPC Results		
Mn (PS)	863	959
Mw (PS)	1136	1686
Pd (PS)	1.31	1.76

ENAMEL FORMULATION

The reduced molecular weight, narrowed polydispersity, and subsequent reduced viscosity of these resins, allow enamels to be formulated with significantly lower VOC. For example, a simple white high gloss baking enamel with the 90% isophthalic Polyester A yields a determined enamel VOC of 2.6 lbs/gal. In the same formula, two of the reduced polydispersity, propylene adipate phthalate type polyesters, AR2 and AR3, are used. Their respective enamel determined VOCs are 2.4 and 2.1 lbs/gal, at the same viscosity. Table V shows the physical properties of the white enamel films for Polyester A, Polyester AR2 and Polyester AR3.

TABLE V

Comparison of Conventional and Stepwise Polyesters

Enamel Properties	Isophthalic Polyester A	Polyester AR2	Polyester AR3
Viscosity, #4 Ford cup (sec.)	40 - 50	40 - 50	40 - 50
det. VOC, lbs/gal	2.6	2.4	2.1
Film Properties (Baked 20 min. @ 350°F)			
Pencil Hardness	4H	4H	3H
Impact (direct/reverse)	60/20	60/20	60/20
60°/20° Gloss	94/80	78/38	70/24
Crosshatch Adhesion, 0 - 5, 5=best	5	5	5
"b" Value Color	-0.2	-0.4	0.0

The properties are quite similar except for the gloss values. The lower values observed for the AR2 and AR3 films forced a closer examination as to how these polyesters respond to common polyester formulating techniques.

It was realized that lowering both the molecular weight and the polydispersity of these resins caused them to behave differently, compared to the 90% isophthalic Polyester A. Specifically, the resins showed differences in both the grinding and the letdown phases of preparation. Consequently, differences were observed in the appearances of the films that were formed. By measuring film properties, both physically and analytically, much was learned about the nature and extent of the differences that these resins showed in response to simple formulating techniques versus Polyester A. As these phenomena were understood, changes in the formulation were made, and these are reviewed in the following sections.

SPECULAR GLOSS

As indicated in the previous section, it was immediately observed that substituting the lower molecular weight polyesters AR2 and AR3, into the simple gloss white formula, produced films with a lower 60°/20° gloss reading than Polyester A. There are several possible reasons for this. First, overcatalysis - which could cause some areas of the film to cure faster than others ("hot spots"). This, in turn, could cause uneven film formation yielding surface defects. Second - catalyst incompatibility - which could cause pigment flocculation, which reduces gloss.[2] Third, poor pigment dispersion - perhaps the result of poor wetting ability of the resins. Fourth, pigment de-wetting during baking - leading to flocculation during cure.

Experimental testing to the conclusion that the initiator was the main problem. The addition of 0.1% of dimethyl ethanol amine (DMEA) improved the gloss.

Scanning electron micrographs were taken of films both with and without DMEA. The high gloss, DMEA containing film was smooth. The low gloss, non-DMEA containing film appeared rough, with definite signs of Benard cell formation. Both of these observations indicate an unstable pigment dispersion and possible flocculation, which lower gloss.[3]

Hence, this small amount of DMEA yields high gloss films by either blocking the catalyst, and/or stabilizing the pigment dispersion. Yet, even though DMEA addition increases gloss, the flow and leveling of the enamel are not as good as Polyester A. Various slower evaporating solvents were also tested to improve gloss and low, but the same low gloss and marginal flow were observed.

CURE STABILITY

As the molecular weight of the polyester was further lowered, from Polyester AR2 to Polyester AR3, the importance of the pigment dispersion phase became more significant. Evidence for this came from the cure stability data. Immediately after preparation, a film of the Polyester A4 enamel cured to an F pencil hardness when baked 15' at 300°F. However, after 24 hours, the same enamel would only cure to a 3B hardness. As time went on, the enamel cured to lower and lower hardnesses, until only a tacky wet film resulted after baking. This indicated that perhaps the curing catalyst was becoming deactivated. The polyester/TiO_2 dispersion was not

sufficiently stable, leading to catalyst adsorption and rendering the enamel incapable of producing a cured, hard film. Such pigment-catalyst interactions have been previously reported.[4]

To remedy this, many pigment dispersants were tested to attempt to eliminate the pigment-catalyst interactions. Of the 30 dispersants tested, only dioctyl sodium sulfosuccinate (DOSS) provided a system with good cure stability, as demonstrated in Table VI.

TABLE VI

Cure Stability on Aging of AR3 White Enamels
Baked 15 min @ 300°F

		Film Hardness		
Catalyst System	Det. VOC (lb/gal)	Initial Bake Out	24-Hour Bake Out	7-Day Bake Out
p-TSA	2.00	<5B	<5B	Tacky Film
p-TSA/DOSS	2.15	H	H	H
p-TSA/DDBSA	2.20	H	H	H

The reason that only DOSS is effective at stabilizing the cure is complex. At first it was felt that it improved and stabilized the pigment dispersion. The DOSS could preferentially wet the pigment surface and remain there to prevent catalyst adsorption in the can. Also, it may remain on the pigment surface to prevent any de-wetting and subsequent catalyst adsorption that may occur during baking. Although this may be partially true, the gloss values remained low, and the flow and leveling properties still gave indications of partial flocculation. The improvement in cure properties was related to the strong acid group contained in the surfactant.

DISPERSION STABILITY

Although DOSS, DNNSA, DDBSA and the amine blocked catalysts impart cure stability to the enamel, they may not aid in pigment dispersion stability. Initially the dispersions show a 7.5 + N.S. Hegman reading and appear glossy, which indicate a good dispersion. However, the cured films have low gloss, marginal flow and leveling, and very noticeable orange peeling. These are all signs of poor dispersion stability. This instability can occur either in the can (room temperature storage), during the shear of spraying, or during the baking process. Yet, it must be remembered that both the higher and lower molecular weight fractions that are characteristic of conventional high solids polyesters have been removed. Evidently the absence of these fractions detracts from the ability of the resin to produce a stable dispersion. Since the commercially available dispersants proved ineffective, it was thought that replacing some of the polyester oligomer with a small percentage of a higher molecular weight, better dispersing resin, would help stabilize the dispersion.

Many types of resins that were known to give excellent dispersions were tested. Two of these, an acrylic (AC1) and a coconut alkyd (AL1) were found to give excellent dispersions. Table VII shows the properties of each of these resins.

TABLE VII

Resin Properties of Coconut Alkyd - AL1 and Acrylic AC1

	AL1	AC1
Resin NV - Percent Solids, Wt.	60	69 - 71
Resin Visc. Stokes	36 - 64	98 - 148
Color	3 max.	5 max.
Specific Gravity 25°C/25°C	---	1.04 - 1.06
Pounds/Gallon, solution	8.7	8.7
Acid Value, on solids	6 - 10	60 - 70
Hydroxyl Value	90 - 110	33
Solvent	xylene	2-butoxy-ethanol
MW	17,391	15,882
MN	2,346	4,815
PD	7.41	3.30

In addition to stable dispersions, these resins also imparted cure stability, excellent flow and leveling, high gloss, minimal orange peel and high depth of image (DOI). Also, scanning electron micrographs (SEM) of films with the coconut alkyd versus ones without it show a smooth film versus a bumpy one. X-ray analysis of these same surfaces show well dispersed titanium in the coconut alkyd containing film, whereas the film without it shows that the bumps contain flocculates of titanium. Tables VIII and IX show the cure stability and gloss improvements over the system without these.

TABLE VIII

Cure Stability of AR3 versus AR3 + AL1, and AR3 + AC1

	15 Min @ 300°F Pencil Hardness			20 Min @ 350°F Pencil Hardness		
Resin	Initial Bakeout	24-Hour Bakeout	4-Weeks Bakeout	Initial Bakeout	24-Hour Bakeout	4-Weeks Bakeout
AR3	5B	<5B	<5B	4H	4H	4H
AR3 + AL1	H	H	H	4H	4H	4H
AR3 + AC1	H	H	H	4H	4H	4H

TABLE IX

Film Properties of AR3 versus AR3 + AL1 and AR3 + AC1

	15 Min @ 300°F				20 Min @ 350°F				
Reason	Pencil Hard.	60/20 Gloss	"b" Value Color	Impact Resist.	Pencil Hard.	60/20 Gloss	"b" Value Color	Impact (D/R)	Det. VOC (lb/gal)
AR3	<5B	---	---	---	4H	82/45	+0.1	80/20	2.1
AR3+AL1	H	95/88	-0.8	120/80	4H	96/89	+1.0	80/20	2.3
AR3+AC1	H	94/85	-0.7	100/60	4H	94/81	-0.4	80/20	2.3

Note that even though these higher molecular resins are used as dispersing aids, the VOC of the enamels is still only 2.3 lb/gal, versus the 2.6 value observed for Polyester A.

The high molecular weight of grinding resins can be directly contrasted to the effect of the high molecular weight fractions of Polyester A (2.6 lb/gal). By examining the molecular weight values for all of these resins, a reason for the above observation becomes apparent.

In Polyester A, the MW and MN are 1584 and 824, respectively. Thirty percent of the chains range between 2649 and 5715 molecular weight (21% on total resin solids), and the white enamel VOC is 2.6 lb/gal. For AR3, MW and MN are reduced to 755 and 567, respectively, with 30% of the chains being 1000-2100 molecular weight, which is less than half the value of the high molecular weight fraction in Polyester A. This difference allows the reduction of the VOC from 2.6 lb/gal to 2.1 lb/gal.

In the coconut alkyd, MW is 17,391 and MN is 2346, with 30% of the alkyd ranging 26,000 to 238,000 molecular weight. When used with AR3, only 5-10% on total resin solids is necessary to give the desired enamel properties. This is much less than the 21% of the higher molecular weight, viscosity contributing material that is present in Polyester A. Hence, although the alkyd improves the enamel properties, it only increases the VOC from 2.1 to 2.3 lb/gal, which is less than the 2.6 lb/gal value for Polyester A. The effect with the acrylic is similar. Its MW is 16,000 and MN is 4815, with 30% of the chains ranging 20,000-71,000 molecular weight.

WEATHERING RESISTANCE

While it has been shown that the enamel physical properties of a conventional high solids polyester (isophthalic Polyester A) are not sacrificed when reducing both the molecular weight and the molecular weight distribution, the weathering properties must also be tested.

It is interesting to compare the QUV performance of the lower molecular weight Polyesters AR2 and AR3 with Polyester A. It is believed that poor pigment dispersion stability is responsible for cure and flow deficiencies in AR3 enamels. However, co-grinding with the alkyd (AL1) or acrylic (AC1) improved the flow and cure stability properties significantly. Based on these results, one might also expect the alkyd and the acrylic to improve AR3 QUV resistance. Yet, Table X shows that this is not the case for the alkyd. Contrarily, the acrylic does give noted improvement. This suggests that there may be a difference between how well these resins protect the pigment surface when exposed to QUV. It has been previously shown that the formation of free radicals from the exposed pigment can be one of the most effective catalysts for resin degradation and poor QUV resistance.[5,6] Coconut alkyds, in general, do not perform as well as acrylics in the QUV. This difference is manifested here when they are co-ground into the AR3 enamels.

TABLE X

QUV Yellowing/Gloss Loss Resistance of Gloss White Enamels
Baked 20 Min @ 350°F

	Initial		112 Hours		240 Hours		544 Hours	
Resin	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color
AR1	93/78	+0.9	76/63	+1.5	75/32	+2.1	54/12	+1.2
AR2	92/68	+0.5	81/46	+2.4	20/3	+2.9	4/2	+2.7
AR3+DOSS	94/75	+0.8	73/35	+4.3	26/4	+4.6	13/2	+4.3
AR3+AL1	92/72	+1.8	77/40	+2.1	49/12	+2.7	8/2	+2.9
AR3+5% AC1	95/89	+0.7	88/65	+0.9	59/21	+1.1	31/4	+2.0
AR3+10% AC1	94/84	+0.7	88/64	+1.9	63/20	+0.7	27/3	+2.0

RESISTIVITY

The conductivity of a polymer and its solutions is generally described as being directly related to concentration and to mobility of ions passing through it under a charge potential. To minimize conductivity of a polymer solution and maximize its inverse or resistivity, it is desired to decrease the concentration or solubility of ions in it. Also increasing the intrinsic viscosity and thus resistance to ion transport raises the resistivity. The latter, of course, is the opposite of what is needed lower the VOC in paints. Thus, removing the high molecular weight fractions as is the case with the stepwise polymers removes that which contributes most to chain entanglement and intrinsic viscosity.

Thus as is the case with high solids polymers and their paints in general, it was desired to raise resistivity by use of non-polar solvents such as xylene, and to thus minimize the solubility of ions such as those of the acidic catalysts within the paints. These approaches were insufficient in the case of the stepwise polymers such as AR2 and AR3. Resistivity in paints such as the

white gloss enamel were still below 0.1 megaohm. The resistivity was considerably lower than would be expected, and this lead to the suspicion that ionic contribution was being made by catalyst residues still bonded to the polyester and thus soluble and conductive in the organic medium.

It was thus desired to raise the resistivity of the stepwise oligomers by use of polyester components which would raise the aliphatic content and provide branching and molecular structure favorable for resistivity. These would also hopefully provide a less favorable media for the solubility of ionic polymeric species.

With the use of branched components inserted into the stepwise oligomers structure, it was possible to prepare paints of high resistivity. In the gloss white enamel formula of the prior illustrations, VOCs below 2.3 lb/gal at 45 sec. #4 Ford Cup were obtained with the oligomers designated AR90 and AR93. Resistivities are on the order of one to three megohms. The paints showed stable cure rates and the resultant films showed high gloss with an excellent combination of hardness and flexibility as well as resistance to accelerated weathering as per Table XI below:

TABLE XI

Oligomers for High Resistivity

	AR90	AR93
NV	97 (1% solvent)	95 (5%)
Viscosity	450 Stokes	250 Stokes
OHV	145	130
White Gloss Formula		
VOC, lb/gal	2.2	2.3
Mega Ohms	2.1	1.5
Viscosity #4 Ford	45 Sec.	45 Sec.
Films 20 Min @ 350°F		
Pencil Hardness	4H	2H
Impact in/lb	60/10	80/20
Gloss 60°/20°	93/83	93/87
After 400 Hrs QUV	67/27	54/18

CONCLUSIONS

The stepwise molecular weight Polyester AR90 is capable of providing an oligomer which will produce films with the same high quality properties as higher molecular weight, lower solids polyesters, at a much lower determined VOC. These low VOCs cannot be achieved by lowering the molecular weights of conventionally produced polyesters. Variations in the properties can be made by the use of pigment dispersants and co-grinding resins. These studies indicate the need for substituting some of the polymer with a better dispersion resin, to obtain the best pigment dispersion, cure stability, flow and leveling, gloss and DOI. This suggests that when removing the low and high molecular weight fractions that are present in conventional high solids polyesters, the resin becomes less capable of giving a stable pigment dispersion.

The regulations are also reported to be changing downward in VOC allowances and it is not clear where they will stop. Table XII below which shows VOC versus paint reduction viscosity indicates that the narrowed molecular weight distribution polyesters maintain or improve their VOC advantage at the higher viscosities.[7,8] The VOC range of 1.3 to 1.5 lb/gal is therefore possible using application equipment designed to spray these higher viscosities. With crosslinkers which would not have emissions by-products VOCs below 1.0 lb/gal might be possible with such equipment.

TABLE XII

VOC vs. Viscosity of Application

Polyester	Trade Name	VOC 50 sec. #4 Ford	VOC 250 sec. #4 Ford
A	Aroplaz 6768	2.6 lb/gal	1.9 lb/gal
	Aroplaz 6755	2.8 lb/gal	2.1 lb/gal
AR2		2.3 lb/gal	1.4 lb/gal
AR90	Aroplaz 6820	2.2 lb/gal	1.3 lb/gal
AR93		2.3 lb/gal	1.4 lb/gal

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New Epoxy/Anhydride Chemistry for Durable, High Solids Coatings

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INTRODUCTION

Heightened concern for the environment across many segments of America has led to increasingly stringent regulations regarding the use of volatile organic compounds (VOC) in coatings, cleaning solutions, adhesives and sealants, refrigerants and fuels[1]. Embodiment of this concern has taken forms as diverse as comprehensive governmental regulations and increased consumer demand for products produced by "green" technologies. Probably the most pervasive of regulations are the Clean Air Act Amendments of 1990 which have brought about major changes in approaches to formulation and application of coatings, among other things.

A survey of trade literature and technical journals in recent years suggests that changes in technology to accommodate lower VOC coating formulations have been rapid and effective. However, in the manufacturing and service sectors of US industry the high cost of capital, high potential product liability and general concern for customer satisfaction comprise a formidable inertia to change coating systems unless there is absolutely no choice in a given situation. Today's regulatory climate provides a powerful economic stimulus to implement new, compliant technologies.

OEM Automotive Coatings

Automotive manufacturing in North America is a microcosm of the general coatings industry. Auto OEMs have their own particular material and capital cost constraints to work within, but in terms of performance, they have the strictest requirements of any segment of the weatherable/durable coatings industry. Coatings which will satisfy automobile manufacturers will likely meet or exceed the performance expectations of all other segments provided that the coating chemistry is applicable to those other segments.

Automotive coatings technologies have undergone substantial change in the last twenty years and will likely see even further change shortly before the turn of the century. A significant shift in performance focus has occurred in the last decade due to increasing liability concerns associated with "environmental etch" -- the physical erosion of coating material on vehicles exposed to acid rain. While acrylic melamine chemistry continues to enjoy favored status in terms of overall material volume applied on North American automobiles, it has become the target chemistry for improvement or replacement by new, "etch-resistant" coating systems in topcoat applications. These new systems present opportunities for suppliers to participate in providing coating systems, raw materials and equipment to manufacturers for future generations of vehicles.

The most prominent recent trend, considering both performance and regulatory factors, is to utilize "high solids" (3.5 lbs VOC/gallon or less) coating systems. For instance, a low VOC electrocoat primer might be followed by a waterborne or powder primer surfacer. Basecoat may be either waterborne or solventborne. The clearcoat, which provides the smoothness, depth and luster to the vehicle can then be applied as a medium to high solids solventborne system with traditional equipment. With this integrated systems approach, total VOCs in pounds per manufacturing site can be controlled by careful production scheduling.

Increasingly strict regulatory requirements will stimulate the evolution of automotive coatings technology in the near future[2]. Technical strategies to meet the demands of lower site emissions include:

1) abatement of emissions "at the stack" after application on the paint line[3]
2) wider implementation of novel application technologies like supercritical CO_2 spray[4]
3) increasing use of non-volatile reactive solvents
4) increasing use of waterborne coatings
5) increasing use of powder coatings
6) reduction in molecular weight/viscosity of coating resins to afford higher solids

Implicit in these strategies are advantages and limitations that will ultimately drive one approach further than the rest as the "best available technology". Strategy one is probably the least attractive due to high capital equipment costs and tax considerations, and general preference for source reduction strategies upstream of the abatement option[5,6]. Strategies two through five will likely produce one dominant driver at some point in the future.

For the present, that leaves strategy six as the most likely area in which immediate coatings system improvements will be made. These improvements will necessarily comprise more than just incremental performance enhancements; cost and product stewardship concerns will be critical factors which must be considered during the research and development phases of new materials.

DURABLE, HIGH-SOLIDS SOLVENTBORNE COATINGS

The following discussion focuses on the application of novel technology to category six -- higher solids solventborne systems via reduced molecular weight/viscosity of system components.

High solids solventborne epoxy/acid and epoxy/anhydride systems for automotive clearcoats began to appear in the literature in the mid to late 80s[7,8]. While there was some established history for the use of "epoxy/carboxy" chemistries in durable coatings applications, this was nonetheless an unexpected challenge to the perceived preeminence of polyurethane chemistry and was especially significant in light of the common perception that epoxy resins (i.e., aromatic glycidyl ethers) don't "weather" well.

Traditional applications of epoxy/acid chemistry in durable coatings include systems as diverse as multifunctional epoxies reacted with dicarboxylic acids, multifunctional (alkyl) acrylic acids reacted with difunctional epoxies and multifunctional (alkyl) acrylic epoxies reacted with multifunctional carboxylic acids[9]. Principal advantages of epoxy/acid chemistry include low raw material cost, excellent film appearance, durability and environmental etch resistance[10]. In addition, the chemistry is versatile enough to produce ambient or elevated temperature cure with common catalysts. Epoxy/acid systems can be applied as solventborne, powder or waterborne coatings.

Traditional applications of epoxy/anhydride chemistry are somewhat more limited. Typical anhydride resins used in durable coatings are comprised of polymers based on maleic or itaconic anhydrides[11]. These are commonly crosslinked by difunctional epoxy resins, multifunctional (alkyl) acrylic epoxies or both. Some references are made to lower molecular weight compounds such as methyl hexahydrophthalic anhydride (MHHPA) being used to crosslink multifunctional epoxies[9, 12], but concerns about the pulmonary toxicity of these materials limits their efficacy in spray applications.

In each of the above cases, the anhydride moiety is a five-membered cyclic structure:

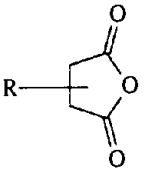


Figure 1. Five-membered cyclic anhydride

However, other permutations of the anhydride linkage are possible; poly alkyl poly anhydrides (e.g., poly adipic poly anhydride) are anhydride-"bridged" linear polymers which can react in the presence of strong nucleophiles to produce polyesters and/or polyamides, for instance.

Another distinct example of the anhydride functional group is a linear linkage as described above, but with one end pendant to a larger structure such as a polymer or oligomer "backbone". Such structures, insofar as their utilization in coatings, were unreported until recently[13, 14]. This paper deals with some of the features of materials which contain linear pendant anhydride (LPA) moieties.

Linear Pendant Anhydrides (LPA)

The simplest representation of this class of materials is seen in Figure 2: the anhydride linkage is terminated by a simple alkyl group (R') on one side, and attached to a central moiety or backbone (R) on the other.

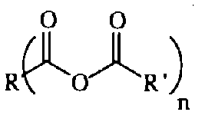


Figure 2. Generic linear pendant anhydride (LPA)

The nature of LPA resins is substantially affected by the structures of R and R' and can be specifically tailored to meet desired performance criteria. For instance, where R is a polymeric backbone, high Tg, high-melting friable solids are easily isolated from process solvents. By contrast, where R is a multifunctional polyester oligomer, lower Tg, low-melting solids can be isolated.

Where R' is methyl, cure with epoxy resins and suitable catalysts can be realized at ambient to bake temperatures; where R' is a higher order residue, such as an isobutyl or t-butyl group, cure is difficult even during extended bake times at high temperatures. LPA resins terminated with substituted alkyl groups can be formulated to stable one-package coatings; partially acylated LPA resins have very high reactivity and relatively short pot lives when formulated as single-package coatings.

FORMULATION AND APPLICATION OF LPA-BASED COATINGS

The following examples comprise actual formulations with spray viscosities, application parameters and coatings evaluation data. A thorough description of each system is included for purposes of illustrating the wide range of binders/crosslinkers which can be utilized.

Additives to the fully formulated systems were based on weight percentages of total resin solids (TRS). Equivalent weights are expressed on a solution basis. All formulations included Tinuvin® 292 hindered amine light stabilizer (HALS) at 1%, Tinuvin® 384 ultraviolet absorber (UVA) at 1.5%, BYK 358 flow control agent at roughly 0.1% and phosphonium catalyst at 2%. Each formulation was "let down" to spray viscosity (35 +/- 1 Zahn #2 seconds) with Dowanol® PMA.

Formulations were spay-applied through a standard siphon-feed pneumatic spray gun to bare polished steel or waterborne basecoat on electrocoated steel. Typical spray parameters were 70 psi line pressure, 6 psi cup pressure. Panels were "flash dried" for 5-10 minutes and then baked at 265-285 deg. F in a forced-air oven for 30 minutes. Physical properties were typically measured within twenty-four hours after bake.

Tinuvin® is a trademark of Ciba-Geigy Corporation
Dowanol® is a trademark of The Dow Chemical Company

Each formulation was measured for actual solids (ASTM D-2369) and contrasted with theory. Discussion of that particular measurement follows the formulation and performance inventory for systems I-VI. Other performance parameters of interest included 20 degree gloss over basecoat, DOI (distinctness of image), Knoop Hardness and Gardner Impact resistance. A brief discussion of durability performance also follows the next section.

Formulation I: LPA Copolymer and Difunctional Glycidyl Ester

The LPA binder was the acetylated product of a 25% (w/w) methacrylic acid copolymer, with a balance of acrylic co-monomers and styrene. Diglycidyl-1, 2-cyclohexane dicarboxylate, a low viscosity liquid epoxy resin, was utilized at 100% solids as the crosslinker.

Component	Weight (g)
Anhydride Binder Resin (66.3% solids; 867 FEW*, solution)	80.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW*)	25.7
Tetraphenyl phosphonium bromide (30% solution)	5.25
Tinuvin 292	0.79
Tinuvin 384	1.18
BYK 358	0.16
Dowanol PMA	38.6
Theoretical system solids = 54.3%	
Measured system solids = 52.8% +/- 1.2	
Zahn #2 time = 35.3 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.69 +/- 0.09 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	84 +/- 1
Distinctness of Image	90 +/- 2
Knoop Hardness	2.9 +/- 0.10
5% NaOH (24 hour spot test)	Pass (no staining or spotting)
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	80 in-lb forward
	20 in-lb reverse

*FEW = Functional Equivalent Weight; EEW = Epoxide Equivalent Weight

Formulation II: Tetrafunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder was based on 40% (w/w) glycidyl methacrylate "loading" in the monomer feed with a balance of acrylic co-monomers and styrene. The theoretical Tg of the GMA copolymer [Fox method[15]] was calculated to be 34 deg. C. The measured Tg [DSC method] was 36.6 deg. C. The LPA oligomer was the acetylated product of pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder Resin (63.9% solids; 534 EEW)	85.3
Tetrafunctional LPA Oligomer (81.0% solids; 340 FEW)	50.0
Tetraphenyl phosphonium bromide (30% solution)	6.33
Tinuvin 292	0.95
Tinuvin 384	1.42
BYK 358	0.19
Dowanol PMA	31.3
Theoretical system solids = 56.6%	
Measured system solids = 54.8% +/- 0.2	
Zahn #2 time = 34.9 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.86 +/- 0.17 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	84 +/- 1
Distinctness of Image	92 +/- 2
Knoop Hardness	7.32 +/- 0.62
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	10 in-lb reverse

Formulation III: Trifunctional / Tetrafunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder used was as described in Formulation II. The LPA oligomer was the acetylated product of a 50/50 weight blend of trimethylolpropane and pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder (63.9% solids; 534 EEW)	84.8
LPA Oligomer Blend (71.9% solids; 413 FEW)	60.0
Tetraphenyl phosphonium bromide (30% solution)	6.49
Tinuvin 292	0.97
Tinuvin 384	1.46
BYK 358	0.20
Dowanol PMA	16.6
Theoretical system solids = 59.7%	
Measured system solids = 57.9% +/- 0.4	
Zahn #2 time = 34.7 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.88 +/- 0.13 mils
MEK Resistance (# double rubs)	200+
Gloss (20 degree over basecoat)	84+/- 1
Distinctness of Image	92 +/- 2
Knoop Hardness	10.5 +/- 0.36
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	10 in-lb reverse

Formulation IV: Difunctional LPA Oligomer and GMA Copolymer

The GMA copolymer binder used was as described in Formulation II. The LPA oligomer was the acetylated product of neopentyl glycol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
GMA Copolymer Binder (63.9% solids; 534 EEW)	79.9
Difunctional LPA Oligomer (81.6% solids; 412 FEW, solution)	50.0
Tetraphenyl phosphonium bromide (30% solution)	6.12
Tinuvin 292	0.92
Tinuvin 384	1.38
BYK 358	0.18
Dowanol PMA	5.9
Theoretical system solids = 66.5%	
Measured system solids = 62.5% +/- 0.3	
Zahn #2 time = 33.8 seconds. Bake 30 minutes at 265 deg. F	
Film Thickness	2.84 +/- 0.29 mils
MEK Resistance (# double rubs to failure)	100
Gloss (20 degree over basecoat)	83 +/- 1
Distinctness of Image	94 +/- 2
Knoop Hardness	6.49 +/- 0.26
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	40 in-lb forward
	<5 in-lb reverse

Formulation V: Tetrafunctional LPA Oligomer and Difunctional Glycidyl Ester

The glycidyl ester crosslinker was defined in experimental formulation I. The LPA oligomer was the acetylated product of pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
Tetrafunctional LPA Oligomer (81.0% solids; 340 FEW)	70.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW)	35.5
Tetraphenyl phosphonium bromide (30% solution)	6.15
Tinuvin 292	0.92
Tinuvin 384	1.38
BYK 358	0.18
Dowanol PMA	36.1
Theoretical system solids = 64.2%	
Measured system solids = 63.9% +/- 0.5	
Zahn #2 time = 34.6 seconds. Bake 30 minutes at 285 deg. F	
Film Thickness	2.83 +/- 0.23 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	82 +/- 1
Distinctness of Image	80 +/- 2
Knoop Hardness	8.13 +/- 0.70
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	40 in-lb forward
	<5 in-lb reverse

Formulation VI: Trifunctional / Tetrafunctional LPA Oligomer and Difunctional Glycidyl Ester

The glycidyl ester crosslinker was defined in experimental formulation I. The LPA oligomer was the acetylated product of a 50/50 weight blend of trimethylolpropane and pentaerythritol reacted with a 50/50 weight blend of MHHPA/HHPA.

Component	Weight (g)
LPA Oligomer Blend (71.9% solids; 413 FEW)	70.0
Diglycidyl-1,2-cyclohexane dicarboxylate (159 EEW)	37.3
Tetraphenyl phosphonium bromide (30% solution)	5.84
Tinuvin 292	0.88
Tinuvin 384	1.13
BYK 358	0.18
Dowanol PMA	13.6
Theoretical system solids = 71.0%	
Measured system solids = 69.9% +/- 0.2	
Zahn #2 time = 35.2 seconds. Bake 30 minutes at 285 deg. F	
Film Thickness	1.85 +/- 0.08 mils
MEK Resistance (# double rubs to failure)	200+
Gloss (20 degree over basecoat)	83 +/- 1
Distinctness of Image	91 +/- 2
Knoop Hardness	6.59 +/- 0.76
5% NaOH (24 hour spot test)	Pass
10% H2SO4 (24 hour spot test)	Pass
Gardner Impact (steel only)	60 in-lb forward
	<5 in-lb reverse

RESULTS AND DISCUSSION

The principal objective of contrasting the previous six experimental formulations was to demonstrate the versatility in enhancing theoretical system solids by making subtle changes in the architecture of the constituent binder and crosslinker resins. LPA resins are inherently simple to design; the ultimate performance goal of a coating system should be achievable by simple experimentation with different LPA structures. Where very high solids (<2.6 lbs VOC/gal) are desired, and where high crosslink density can be tolerated, a system such as experimental formulation #6 is feasible. Where a softer, more flexible coating formulation is desired, and where higher VOC levels can be tolerated, a system such as experimental formulation #1 is indicated.

Table I summarizes the six experimental systems, and a "standard" polyester polyol / HDI trimer polyurethane system from the perspective of formulation solids at roughly comparable viscosity. The systems are rank-ordered from lowest solids to highest solids, with no other performance parameters considered. Numbers in parentheses under System / Description indicate the theoretical functionality of the LPA oligomer(s).

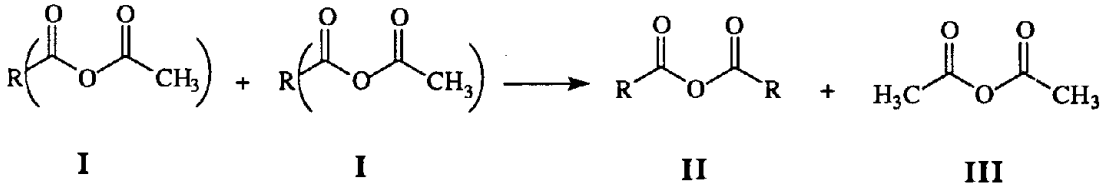
Table I. Rank-Order of Experimental Formulated Systems by Theoretical Solids

System / Description	Zahn #2 Viscosity (sec.)	Theoretical Solids (% w/w)	Measured Solids (% w/w)
#1 - LPA Polymer / diglycidyl ester	35.3	54.3	52.8 +/- 1.2
"Standard" - Polyester polyol / HDI Trimer Polyurethane	34.3	54.9	54.8 +/- 0.0
#2 - LPA Oligomer (4) / 40% GMA Copolymer	34.9	56.6	54.8 +/- 0.2
#3 - LPA Oligomer (3 + 4) / 40% GMA Copolymer	34.7	59.7	57.9 +/- 0.4
#5 - LPA Oligomer (4) / diglycidyl ester	34.6	64.2	63.9 +/- 0.5
#4 - LPA Oligomer (2) / 40% GMA Copolymer	33.8	66.5	62.5 +/- 0.3
#6 - LPA Oligomer (3 + 4) / diglycidyl ester	35.2	71.0	69.9 +/- 0.2

With concern for VOCs in coating formulations being a primary driver for new technology development, the delta between theoretical and actual (measured) solids in the experimental systems deserves some attention. In effect, there are two primary forces at work which lead to a loss of some of the system "solids": 1) volatility of the constituents and 2) self-condensation of LPA functional groups to form an intermolecular linkage and liberate a volatile symmetrical anhydride. Both phenomena lead to an undesirable increase in measured VOC and are related to the degree that each exacerbates the other.

In formulations such as #1, #2, #3 and #4 where one of the constituents is a polymer, fast vitrification of the film leads to a higher probability of unreacted low molecular weight material vaporizing from the matrix. This is nicely contrasted in formulations #1 and #4 where each system has a two-functional component. System #4 in particular loses 4% of its theoretical solids due to the loss of the volatile two-functional LPA molecule. System #1 utilizes a less volatile two-functional diglycidyl ester, which nonetheless will volatilize when tested alone by ASTM D-2369.

In the second situation described previously, the LPA functional group can condense with itself to liberate a volatile symmetrical anhydride, acetic anhydride (III) in the cases of the resins formulated for this study:



I I II III

Figure 3. Self-condensation of LPA molecules.

It is not clear at present how the kinetics of this reaction relate to the desired reaction (LPA addition to oxirane); further studies should elucidate these differing features. For the present, it has been established that higher catalyst levels minimize the delta between theoretical and measured solids.

In systems which are lower in net functionality (formulations #5 and #6) due to the absence of polymeric constituents, better mixing and thus distribution of reactive moieties is possible. However, lower molecular weight equates to higher volatility and higher functional group loadings. The net result of this is a high "attrition potential" of acetic anhydride (III) from systems #5 and #6. 13.5% and 10.0% of these systems could be lost, theoretically, if the reaction depicted in Figure 3 were the predominant reaction rather than addition of LPA to oxirane.

As self-condensation progresses system stoichiometry becomes unbalanced, again leading to a higher probability of unreacted low molecular weight material (diglycidyl ester in this case) vaporizing from the matrix. The fractional deltas determined experimentally for these two systems (0.3 and 1.1%, respectively) suggests that self-condensation is a minor deficiency of this chemistry that can likely be overcome by system optimization, primarily as it relates to catalysis.

Other properties measured in this study suggest that coatings based on LPA and epoxy will fulfill typical requirements for high performance coatings, i.e., excellent appearance (gloss and DOI), solvent resistance and flexibility (extrapolated from Gardner Impact). No optimization of these experimental formulations was attempted for this study.

DURABILITY

One of the key required features for automotive coatings is durability -- the resistance of such coatings to environmental attack, including sunlight (UV radiation), oxygen, heat and moisture cycling, acid rain, bird and bug droppings, tree sap, etc. Current expectations for OEM automotive coatings in particular are that they will maintain both physical integrity and excellent appearance for the normal service life of the vehicle.

In the present study, durability testing requiring extensive investment of time was not possible. However, Figure 2 represents accelerated durability testing by QUV® 313b conducted in this laboratory for analogous formulations. The curves depicted in the graph represent average 20 degree gloss readings for six panels distributed randomly in two QUV cabinets. Error bars are not included, nor are the ordinate values expressed as percent retention of initial gloss, because the time to failure of these systems is substantially different from one another.

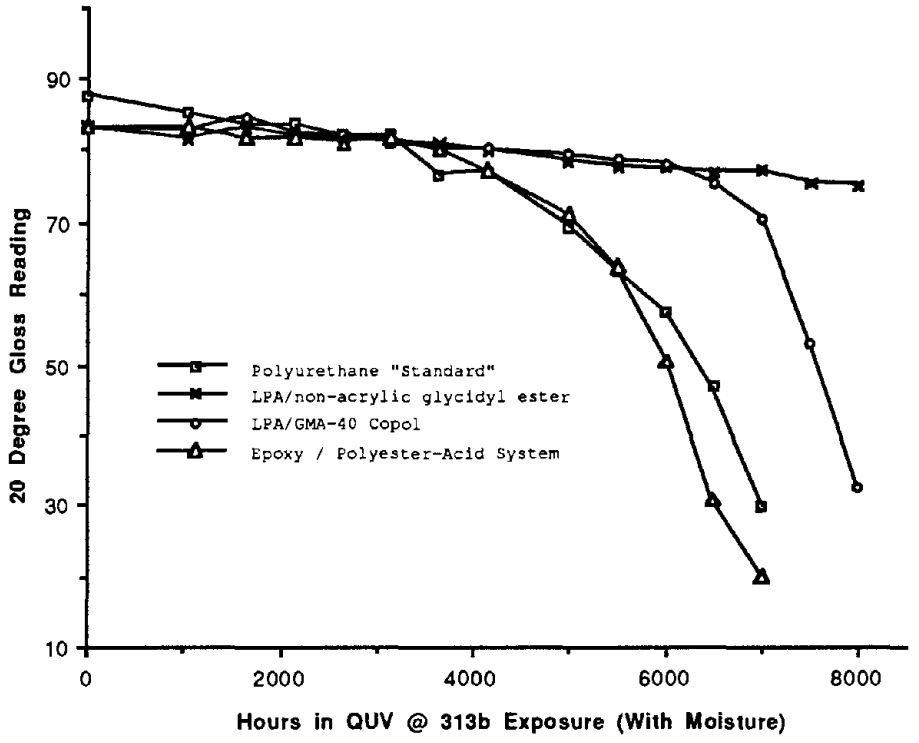


Figure 4. Gloss Retention of Epoxy / LPA Systems Versus "Standards" in QUV Testing

For the purposes of this study, four systems have been represented: 1) polyester polyol/ HDI trimer polyurethane "standard" [experimental system #7)], 2) LPA oligomer / glycidyl ester system [similar to experimental systems #5 and #6], 3) LPA oligomer / 40% GMA copolymer [experimental system #2] and 4) 40% GMA copolymer with saturated acid-functional polyester crosslinker. Each system was stabilized as reported for the experimental formulations in this study: 1% HALS and 1.5% UVA by weight based on total resin solids. The testing cycle was 4 h UV/60 deg. C, 4 h CON/50 deg. C as per ASTM D-4587.

QUV® is a trademark of The Q-Panel Company, Cleveland, OH

A cursory analysis of Figure 2 suggests that while "standard" polyester urethane and epoxy / acid clearcoat systems have excellent durability in this test to about 5000 hours exposure, the two LPA-based systems have even greater durability. System #2 was removed from the test condition after 9600 hours with over 70% retention of initial gloss. None of these test systems was optimized, although previous extensive experience with the polyurethane system led to its adoption as the "standard" for comparative purposes in this ongoing testing program.

CONCLUSIONS

In an effort to address the major driving forces for new technology development in durable coatings applications, a new epoxy-based chemistry was introduced. Performance standards for automotive coatings were chosen as a target in an evaluation of typical coating performance parameters including appearance, flexibility, solvent resistance and durability in accelerated laboratory testing. Perhaps the most important picture this study paints for the research community is that epoxy-based coatings, traditionally thought of as non-weatherable, are very durable while meeting all other requisite performance criteria.

Driving forces to lower VOC levels in paint systems while improving appearance, durability and reducing or minimizing cost will continue to force the evolution of new technologies. "Epoxy / carboxy" chemistry, one of the newest challengers in the marketplace, is substantially qualified to address these driving forces. In particular, linear pendant anhydride (LPA) / glycidyl ester technology offers tremendous latitude in binder / crosslinker architecture to address solids, flexibility and durability.

Very high solids formulations (< 2.6 lbs. VOC / gal) applicable to traditional application equipment are possible with this chemistry. Future work will explore alternative application methods for LPA-based systems. Exploration of system improvements will focus on laboratory evaluations of etch resistance and scratch / mar performance relative to standard paint systems.

ACKNOWLEDGMENTS

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SESSION 10

LOW- AND NO-VOC COATINGS-PART 2

PAPERS PRESENTED:

"100% Solids Liquid Sprayable Coatings"
by
David Grafflin
Tioga Coatings Corporation
Calumet City, Illinois

"Alternative Dielectric Coating Medium for Electric Motor Field Coil Manfacture"
by
William Herz
University of Alabama
Tuscaloosa, Alabama

"Odour and VOC Emissions Reduction on Coil-coating Lines by Using Waterborne Paints- Part II: Full Waterborne System Application"
by
Serge Vigneron
Société Belge de Filtration
Louvain-la-Neuve, Belgium

Closing Remarks
by
Michael Kosusko
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Research Triangle Park, North Carolina

100% Solids Liquid Sprayable Coatings

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Introduction:

This paper covers a series of environmentally compliant liquid coatings, with a primary emphasis on the first commercially available 100% solids liquid sprayable baking coating. The application and performance characteristics of this technology, along with companion compliant coatings materials developed to fulfill other coatings technology niches will be discussed. Given the focus of this conference, the availability of these materials provides significant economic advantages for the liquid coatings end-user who is facing regulatory pressures and needs to consider alternatives for compliance which provide required levels of performance while addressing existing and proposed regulations on VOC's, HAPs content, and SARA 313 reportable constituent issues, while at the same time not requiring full-scale equipment conversions.

Virtually the entire industrial coatings-related community [raw material suppliers, chemicals and coatings manufacturers, and end users] have watched with great interest the development of (and the lack of uniform enforcement of) the Clean Air Act of 1990 and its Amendments. While there once appeared that there would be wide-spread general enforcement of these regulations across industry segments and geographies, certainly the record to date has been one of localized limited activity, most typically the result of specific incidents or local (state level) interest. The initial implications of the regulations, however, have prompted re-alignments in technology development by suppliers to the coatings industry, and the ensuing years have seen some distinctly different formulation approaches taken to providing the end users of paints and coatings with environmentally friendly alternatives. This conference has been organized to focus on those liquid compliance coatings technologies which are commercially available or under advanced development, and to identify which can provide end users the technology they need to maintain their requirements for product performance while addressing current or proposed environmental regulations without the necessity for add-on control equipment (incinerators, thermal oxidizers, etc.) or wholesale conversion of existing application equipment.

Several years ago, certainly before a significant pretense of regulatory pressure began to emerge, one of the first major compliance alternatives to conventional solvent-borne liquid coatings came in the introduction of powder coatings. While capable of providing an option in many situations, a conversion to powder from liquid always requires rather considerable equipment expense, often in the range of hundreds of thousands of dollars. While it provides an escape from the VOC issue, the use of powder coatings leaves the end user to

CHART ONE: Comparative Features And Benefits Summary Chart

Product Features	TioTech 20	TioTech 21	Powder	Solv. Hi Solids	Water Hi Solids
Differentials In Solids As Supplied	100%	87-94%solids	100% solids	60-65%solids	50-55% solids
Differentials In First Pass Transfer Efficiency	90%	85%	55%	85%	85%
Specific Product Attributes					
Low cost/AccCpplied Film Build (0.5-1.0 mils DFT)	yes	yes	no	yes	yes
Potential 75% Reduction In Heated Make-Up Air Requirements	yes	no	yes	no	no
No Additional Application Or Cure Equipment Investment	no	yes	no	yes	no (st. steel)
Faster Line Speed (No "Flash Off" Zone Needed)	yes	no	yes	no	no
Minimal Waste Disposal Cost	yes	yes	yes	no	no
No Product Capacity Limits Due To Current VOC Allowables	yes	yes	yes	no	no
Color Changes In Less Than Two Minutes	yes	yes	no	yes	yes
Reduced Need For Explosion-Proof Equipment	yes	no	yes	no	no
Reduced Need For Extensive Fire Sprinkler Systems	yes	no	yes	no	no
Multiple Color Overspray Is Recyclable	yes	no	no	no	no
No Need For Separate Paint Room/Reduced Manpower Costs	yes	no	yes	no	no
Lower Shipping Costs With No Solvent Or Water Shipped	yes	no	yes	no	no
No Need For Special Weather Formulas/Solvent Purchases	yes	yes	yes	no	no
Lower Scrap Rates Due To Accurate Wet Film Measurement	yes	yes	no	yes	yes
No Need For Refrigerated/Humidity Controlled Storage Area	yes	yes	no	yes	no
Excellent Film Control Due To Lack Of "Fines"	yes	yes	no	yes	yes
No Solvent Or Co-Solvent, Eliminates LEL/LFL Concerns	yes	no	yes	no	no
Overspray/Plant Contaminated Material Is Filterable	yes	yes	no	no	no
Meets All Existing/Proposed Environmental Rules On Emissions	yes	yes	yes	no	no
Number of "Yes" Issues	**18**	**11**	**11**	**6**	**4**

deal with the issues of difficult control of thin films, lack of quick or easy color changing without extensive dedicated equipment, the unavailability of blending systems which can make short runs

of custom colors effective, the tendency to build thick films on cut edges, and all of the other characteristics which are typical of powder coatings technologies. As environmental pressures increased, on the liquid side, the initial compliance alternative was water-borne coatings. The technical definition of water-borne materials does not equate to a lack of solvent, and in many cases, while solvent levels are lowered in water-borne formulations, they may not be lowered to a point that they will not be the subject of the first round of serious control requirements. Utilizing a partial introduction of water as a diluent in these materials, resulting in a VOC level which is still in the vicinity of 3.0 pounds per gallon, does not provide a meaningful alternative. Keep in mind, there are many excellent conventional high solids solvent-borne materials available today which routinely are capable of providing VOC levels in the 2.5 pounds per gallon range. In all fairness, however, there are a number of water-borne materials available in a variety of resin technologies for application on metals and plastics which are both water-borne and zero VOC. A drawback shared by all of these water-borne materials is the requirement for equipment modifications including grounding and isolation of equipment for electrostatic application, the use of stainless steel fittings to avoid premature corrosion and system failure, and a tendency for the overspray of these materials to be somewhat more difficult to clean up due to a tendency to remain tacky for an extended period of time on booth walls, conveyor hooks, filter sections, etc. As a result, in many regions, the disposal of waste materials including water-borne coatings residue is becoming increasingly expensive and difficult to arrange.

An alternative approach to the concept of compliance in liquid coatings was taken, however, in considering looking at systems for which the vehicle could be the basic resin itself, rather than either solvent or water. This novel approach, which at first blush might appear to be almost a chemical oxymoron, was intended to develop materials which could be described as 100% solids, liquid, sprayable coatings. While many may have considered the potential for creating materials of this sort, the technical persistence and innovation which have made this possible are the result of an extensive evaluation of formulation alternatives, the willingness to consider unique combinations of materials and their processing, and an essential understanding of the breakthroughs necessary to make this successful. Significant re-engineering of existing technologies on this level is not accomplished by attempting to "tweak" conventional high solids coatings. Those materials, while very competent in their current state, rely on the presence of a level of solvents in order to maintain their stability, and do not lend themselves to this kind of modification.

As the effort for commercialization of a material of this sort came toward success, certain characteristics of this emerging technology became better defined. In the absence of conventional diluents, it is not surprising that these materials are typically higher in viscosity than their traditional counterparts. As compared to a traditional material which might exhibit a viscosity of 500 centipoises, the first iterations of this new technology emerged at levels above 10,000 centipoises. Over time, subsequent revisions of this basic chemistry have lowered package viscosity to levels below 6,000 centipoises at room temperature, still somewhat thicker than traditional materials. For purposes of comparison, this approaches the room temperature viscosity of pure maple syrup.

Material viscosities at this level can generate some understandable concerns in fluid handling. In a traditional material with this sort of consistency, it would be virtually impossible to move the material through fluid lines or application equipment with any realistic level of control. In these formulations, however, an inherent understanding of their thixotropy (the property of highly viscous materials to become more fluid as they are heated, shaken, stirred, etc.) is necessary. The unique response of these materials to the mechanical influences of agitation, shear and temperature translate to the development of excellent fluid management and spray application characteristics. On high speed rotary atomizers (disks, bells, etc.) typically operating at 35,000 rpm or higher, application at either room temperature or very slightly elevated temperatures (less than 110F.) results in an ability to apply controllable thin films with excellent coverage,

electrostatic wrap, flow and levelling. The advantage of utilizing heat in the range of 100-110F. is the assurance of uniform fluid flow rates year-round due to uniform material temperature regardless of changes in ambient plant environment. As heat is introduced to the coating, the addition of every twenty degrees Fahrenheit sees an associated reduction in viscosity of fifty percent. Keep in mind that conventional solvent-borne materials, which are much lower in initial application viscosity, undergo evaporation of the solvent as they travel through the air from the application equipment to the part being painted, resulting in a material which arrives at the part fairly high in viscosity, and one which (therefore) does not exhibit sags or runs. The materials which are the focus of this presentation react to the shear created by the rotary atomizers by lowering their viscosity in flight, but then regain their viscosity on the part, similarly preventing sags or runs. These coatings, given their solvent-free make-up, maintain essentially all of the electrostatic charge to which they are introduced, resulting in outstanding first pass transfer efficiencies (routinely measured at numbers above ninety percent when applied on high-speed rotary atomizers) and associated excellent wrap properties as they are applied. This combination of characteristics provides a material which typically requires significantly less reinforcement or touch-up than more conventional solids materials. In addition, if there is a desire to apply these materials to embossed metal surfaces, the rheology of the coatings can be modified to provide a coating which will coat the coined or embossed surface uniformly, with excellent sag control on the flat surfaces of the pattern and "hang" on the edges of the valleys, without material flowing away from the edges and/or filling the pattern. The cosmetic results of this sort of application rival any of the more conventional solids liquid materials which have been used for some time, and exceed the capabilities of powder coatings in applications on embossed surfaces.

CHART TWO: First Pass Transfer Efficiency Numbers By Application Method

Application Equipment	Transfer Efficiency On Small Targets	Transfer Efficiency On Large Targets	**Definitions:**
Conventional Air	15%	40%	Large Targets:
Conventional Air Assisted Airless	30%	60%	Doors, partitions,
Conventional Airless	20%	50%	desks, shelving, etc.
Conventional HVLP	30%	45%	
Electrostatic Air	40%	65%	Small Targets:
Electrostatic Air Assisted Airless	45%	75%	Wire goods, tubular
Electrostatic Airless	45%	75%	furniture, hardware,
Rotary Atomizers-H. S. Disks	85%	95%	etc.
Rotary Atomizers-H.S. Bells	80%	90%	

The coatings developed in this work truly represent a unique chemistry. In performance, they resemble most closely the properties and characteristics of a modified polyester film. These are one-pack materials which cross-link with heat to form a film. In line with the commitment to provide materials with optimum environmental responsibility, these formulations contain no heavy metals, do not contain materials on the HAPs inventory, have no SARA 313 reportables and have no VOC's as supplied.

On the subject of VOC's, however, some clarification of this issue is required. While the individual components of these coatings when compiled into the finished material are of a nature that no VOC's are reportable in the initial package, if one runs either ASTM method D-2369 or EPA Test Method 24 on these products, some volatiles are given off. In these test methods, about 0.3 grams of coating is placed in an analytical testing pan and weighed. It is then heated to 110C. for one hour, and re-weighed to determine the degree of weight loss. The weight loss represents

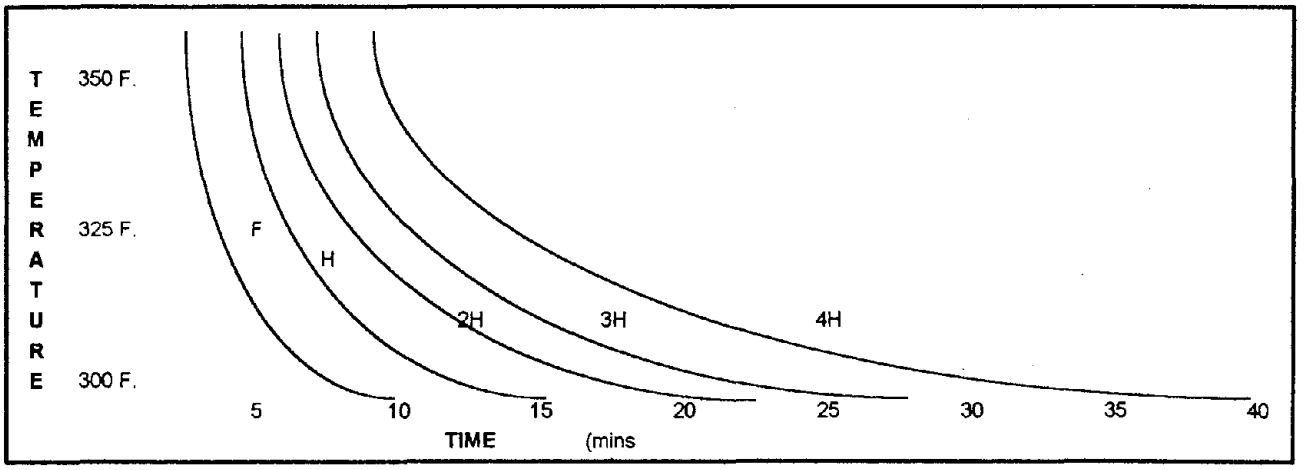
what are identified as volatiles. The 100% solids version of this chemistry, when evaluated with these test methods, shows a material loss which calculates to approximately 0.8 pounds per gallon VOC's. What has volatilized during the test are low molecular weight organic materials. These are not conventional solvents being removed from the formulation, these are formulated materials whose components in the lowest molecular weight region are being given off. It should be noted, this same phenomenon with a measurable loss of volatile contents occurs in the cure of powder coatings, again despite the complete lack of conventional solvents in their formulation.

Other characteristics of these materials deserve attention as well:

Gloss: typical formulations can be provided at gloss levels between 20% and 90% when read on a 60 degree gloss meter. If one attempts to formulate materials much below 20%, the additions of the necessary flattener to achieve a true matte finish can have a dramatic effect on increasing the viscosity and render the material very difficult to manage.

Pencil Hardness: Depending on the length of the cure cycle at a stated temperature, significant differences in pencil hardness can be observed. For instance, in conventional convection cure ovens at a 325F. cure temperature, a pencil hardness of "F" is measured after 6 minutes of exposure, while a pencil hardness of "4H" is measured after 14 minutes at the same temperature. At a 350F. cure temperature, a four minute cure cycle will provide an "F" pencil hardness, while a nine minute exposure will provide a "4H" pencil hardness. In the high heat conditions present in a coil coating oven (30 seconds or so at a peak metal temperature of 435-450 F.), H-2H pencil hardness is accomplished within these typical cure parameters. Keep in mind, cure can begin very quickly as no solvent has to be removed from the film prior to beginning the cross-linking process. The attached graph summarizes this relationship between time, temperature and pencil hardness in a conventional convection oven.

CHART THREE: Cure Characteristics (Time Versus Temperature)



Exterior Weathering: when these coatings are placed on traditional exterior exposure without the use of a primer, the films do not yellow, crack, craze, blister, pit or delaminate. However, the films do exhibit some loss of gloss and develop a level of chalking. Currently, in order to pass more stringent exterior exposure requirements, materials that meet these needs require the application of a companion environmentally compliant primer. A conversion of this product to a single-coat technology is in its final stages of development, but all work to date indicates that as a two-coat system, these chemistries will provide excellent weathering characteristics for a wide range of applications. This is not to indicate that in this current state they

will be able to match the exterior exposure performance of traditional PVDF films with ceramic pigmentation, which remain the benchmark of high-performance exterior exposure. It is the intention of the research effort underway to be able to provide this weatherable material in a single package, single-coat material.

Corrosion Resistance: in typical salt spray and humidity testing, these materials demonstrate the range of performance one would typically associate with their more conventional counterparts (1/8" maximum creep from scribe at 500 hours over Bonderite 1000/Parcolene 60 treated cold rolled steel). As with more conventional solids materials, this performance can be dramatically affected by the selection of pretreatment processes which are utilized prior to their application. As indicated previously, the use of an associated primer, or the use of two coats of this material, will also enhance properties related to corrosion resistance.

Hiding Properties: these materials will provide excellent hiding at and below 0.5 mils dry film thicknesses, depending on the color being applied and the shape and contour of the parts being painted. In addition, the combination of hiding properties and electrostatic wrap discussed earlier typically allows the end user to enjoy a significant improvement in overall film requirements versus appearance when compared either to more conventional solids liquid materials or to powder coatings. It is very difficult to control powder coatings consistently at films under 2.5 mils, while this material can be easily maintained at less than 0.5 mils if desired. It should be noted that in order to obtain optimum performance from the liquid materials, typical dry film thicknesses are in the range of 0.8-1.0 mils.

Flammability: this material, in its 100% solids version, does not have a measurable flash point. As you start to heat it much past 200F., the coating begins to cure. As a result, it is rated as a Class III-B combustible for purposes of transportation and storage, the same classification as powder coatings.

Settling: Referring back to the discussion of thixotropy, these materials do not settle in the traditional fashion. Therefore, continuous agitation is not required as it would be with a more traditional material. As a result, the normal paint kitchen set-up with timed agitation, etc., is not required, and this material can, in fact, be stored immediately next to the spray booth, shortening supply lines and reducing the necessary circulation equipment.

Required Minimum Air-Flow: the application of any coatings requires some level of air to be moved past the operators and through the spray area. These materials, like powder coatings, do not require the same levels of air make-up or flow as more conventional materials, which can generate a variety of process benefits. Not only does the lesser use of air reduce the cost of heating air and controlling the paint room environment, the physical reduction in air-flow through the spray area can lessen the potential for dust and dirt contamination to be blown onto the applied but uncured film. In addition, the sizing of new equipment to comply with insurance regulations on operator safety becomes less complex when this material is utilized exclusively.

Reclaim of Overspray: in a clean room environment, overspray can be captured and recycled with no loss of properties as there is no solvent being lost which needs to be reconstituted. If dust or other contaminants are a problem, the material may need to be filtered prior to re-use. In addition, if there is a suitable application for a blended color, all of the overspray can be collected in a single holding tank, blended together under simple agitation to create a single color, with complete compatibility, and re-applied as needed. The capability to collect overspray and to re-use it either by itself or in conjunction with companion materials in a blend is not shared with powder coatings, where the only reclaim option is to isolate all materials individually, and to assure that there has been no cross-contamination of either the equipment or the coating in order for it to be re-used.

Shelf Life: there are no particular differences in the storage of this material as compared to a high-quality conventional coating. It is warranted for storage in unopened containers for twelve months from the date of manufacture, and only requires normal cautions in its handling. After the twelve month period, we do reserve the right to evaluate the material to assure that nothing unusual has been done with the coating in the interim.

With this information as a background, what about those end users who face a desire to find a compromise between remaining with conventional high solids materials and current application equipment and going to 100% solids material, and the potential for having to install equipment modifications (which may range from merely the installation of line heaters to the use of larger feed lines and fluid handling equipment to adapt to the higher viscosity of the full-strength materials or the transition to state of the art application equipment)? In these cases, there is a product option available which provides a significant reduction in VOC's while allowing the continued use of existing application equipment.

CHART FOUR: Comparative VOC's Chart

Category of Comparison	Conv. Solids	Conv. High Solids	Ultra-High Solids-No. 1	Ultra-High Solids-No. 2	Ultra-High Solids-No. 3
VOC Levels/Gallon	4.0 lbs.	2.8 lbs.	1.5 lbs.	1.0 lbs.	0.5 lbs.
Approximate Volume Solids	40%	60%	77.50%	85%	92.50%
Sq. Ft./Gal. @ 1.0 mil (theoretical)	640	960	1240	1360	1480
Sq. Ft./Gal @ 50% First Pass Tr. Eff.	320	480	620	680	740
Gallons To Cover 1.0MM Sq. Ft. @ 1.0 Mil	3,125	2,083	1,613	1,470	1,351
VOC's On 1.0MM Sq. Ft @ 1.0 Mil	12,500 lbs.	5,832 lbs.	2,419 lbs.	1,470 lbs.	676 lbs.
% VOC's Vs. 40% Vol. Solids Coating	100%	46%	19%	12%	5%

Based on 1.0MM sq. ft. at 1.0 mil dry film

This second family of materials is created by taking the 100% solids coating and introducing a small amount of non-HAPs solvents to create a significantly less viscous material (the impact on viscosity of low levels of diluent is remarkable). As summarized on Chart Two, the resulting coating has all of the properties of its 100% solids counterpart, but in a package which allows easier application on existing manual or automatic spray equipment. The amount of dilution can be monitored, depending upon equipment requirements, to provide a material which ranges in calculated VOC's from just over 1.0 pound per gallon to approximately 2.5 pounds per gallon (including cure by-products), or 0.5 to 1.5 pounds per gallon as supplied.. An option this material provides, in addition to being essentially a "plug-in" process change, is a mechanism whereby a significant reduction in VOC's can be implemented almost immediately, as a demonstration of a significant commitment to environmental compliance without having to make a large initial capital investment in advance. While many of the issues relating to equipment changes can be eliminated by the choice of the super high solids materials, keep in mind that this option with its use of solvent brings back into play the need to store this material like its more conventional counterparts and to maintain a higher level of booth air make-up and exhaust than the more compliant material.

CHART FIVE: Typical Physical Properties

	TioTech 20	TioTech 21
Weight Per Gallon:	9.4 to 14.0 pounds	9.0 to 13.5 pounds
Weight Solids:	100%	84% to 96%
Volume Solids:	100%	80% to 93%
Theoretical Coverage At One Mil Dry Film Thickness:	1600 square feet	1280-1488 square feet
Color/Gloss:	Matched To Standard	Matched To Standard
Flash Point:	Greater than 200F.	Greater than 100F.
Shelf Life:	Twelve Months	Twelve Months
Pencil Hardness:	H - 4H	H - 4H
Stain Resistant To:	All Standard Stains	All Standard Stains
Adhesion to Cold-Rolled Steel:	100% cross-hatch	100% cross-hatch
Mar Resistance:	Excellent	Excellent
Flexibility:	Pass 1/8" mandrel	Pass 1/8" mandrel
Direct Impact:	Pass 120 inch-pounds	Pass 120 inch-pounds
Salt Spray (500 Hours):	1/8" creep	1/8" creep
Solvent Resistance: 200 MEK Double Rubs	no apparent effect	no apparent effect
Solvent Resistance: 200 Xylene Double Rubs	no apparent effect	no apparent effect
Automotive Fluid Resistance:	no apparent effect	no apparent effect
(after 16 hours immersion):	no apparent effect	no apparent effect
	no apparent effect	no apparent effect
	no apparent effect	no apparent effect
Taber Abrasion: 500 cycles/500 grams/CS10 wheels	0.02 grams	0.02 grams
Tested On Bonderite 1000/Parcolene 60 Substrate		

As an example of the levels of impact this technology can have, in a typical industrial high volume facility, utilizing a conventional (40%) solids material, it would not be unusual to generate 750 tons per year of VOC's. In a transition to high (60%) solids material, this number would drop to approximately 345 tons per year of emissions. However, in a transition to the super high (85%) solids, this number moves down to a level approaching 100 tons per year, and a move to the 100% solids material can lower the number to less than 60 tons per year, with all of these volatiles coming from the resin component, not from any solvents or other traditional organic constituents.

From almost any perspective, the availability of these levels of VOC reduction can allow not only the resolution of virtually any environmental concern tied to emissions, but in this age of regulatory balancing, can provide the opportunity for emission offsets (where these are available) to support the installation of other processes within the manufacturing operation which while not paint-related, may generate measurable VOC's of their own, and thus impact some of the issues related to air permits.

CHART SIX: Comparative Systems Costs - Liquid Vs. Powder Coatings

CONVERSION JUSTIFICATION EXAMPLE	Powder Coatings	TioTech 20
Volume Solids	100%	100%
Potential Material Utilization (with overspray recovery)	95%	95%
Typical Solid Density (both with same "light" color)	14 lbs./gallon	14 lbs./gallon
Typical Quoted Price (Computed Equivalent Price)	$2.50/lb. OR $35.00/gal.	$35.00/gal. OR $2.50/lb.
Dry Film Thickness Applied	1.5 mils	0.75 mils
First Pass Transfer Efficiency	55%	90%
Cost/Square Foot At First Pass Transfer Efficiency	0.0595	0.0182
Cost/Square Foot At Potential Utilization	0.0344	0.0172
Cost Savings Versus Powder:		
Based on first pass efficiency:		69%
Based on potential utilization:		50%
cost per square foot = $/gal. x mils/16.04 x % efficiency		

Example of potential payback justification:

IF powder purchases equal:	$1,000,000 per year
TioTech 20 usage @ 50% savings level would be:	$500,000 per year
Gallons purchased @ $35.00/gallon would be:	14,286 gallons per year
Daily usage @ 52 5-day weeks would be:	55 gallons per day

If the equipment cost to convert to a one drum per day 100% solids liquid spray application is less than $500,000 - the payback would be less than one year.

Therefore:
Converting to a 100% solids liquid would then result in a net operating profit of $500,000 below the line for every future year following the year of installation.

An additional topic which should be mentioned at this point of the conversation is economics. For too long, a myth has surrounded powder coatings that they represent not only the environmental alternative for those confronting some of these issues, but are also the low-cost choice - in reality, once liquid coatings move up to ultra-high solids levels, the economics begin a dramatic shift.

Not surprisingly, when development work of this sort is undertaken, avenues of technology are uncovered which can lead to a variety of additional compliant materials. Among the other variants of the super high/100% solids materials is a companion 100% solids material which can have application as a primer-surfacer in the automotive industry. The automotive exterior coatings market, as you know, typically utilizes a high-build cathodic electrodeposition primer as a foundation over pretreatment and ends up with a color coat or color coat/clear coat combination on top of it. In-between, while the trend had been away from the use of a primer-surfacer to act as a higher dry-film buffer between the primer and color coat, for a variety of reasons ranging from levelling to corrosion resistance to control of color development, greater attention is being given to the use of a barrier coat. In many cases, air permits have been re-written to reflect the absence of this layer, so the availability of a low or no VOC material for this application can be evaluated without having to re-open an air permit modification caused by the consideration of a low solids material of the sort previously utilized. It should be noted that there is currently no intention to consider these materials as automotive exterior body color materials, both due to the issues of cost and of weathering data versus the current chemistries being utilized, and due to the historical dominance and support data tied to the existing suppliers and their materials.

Remaining in the general industrial coatings arena, a material has been developed which is a zero VOC water-borne air dried material for applications on metals, etc. This material formulates at approximately 40% volume solids, has no measurable flash point, and if thinning is required, it can be done with tap water. This material is very forgiving of reasonable levels of surface contaminants, and will demonstrate excellent adhesion over various clean surfaces, with or without subsequent pretreatment. After 24 hours of air drying, or a short period of force drying (30 minutes at 150F or so), this material exhibits reasonable hardness and excellent film flexibility, impact resistance, and other physical properties.

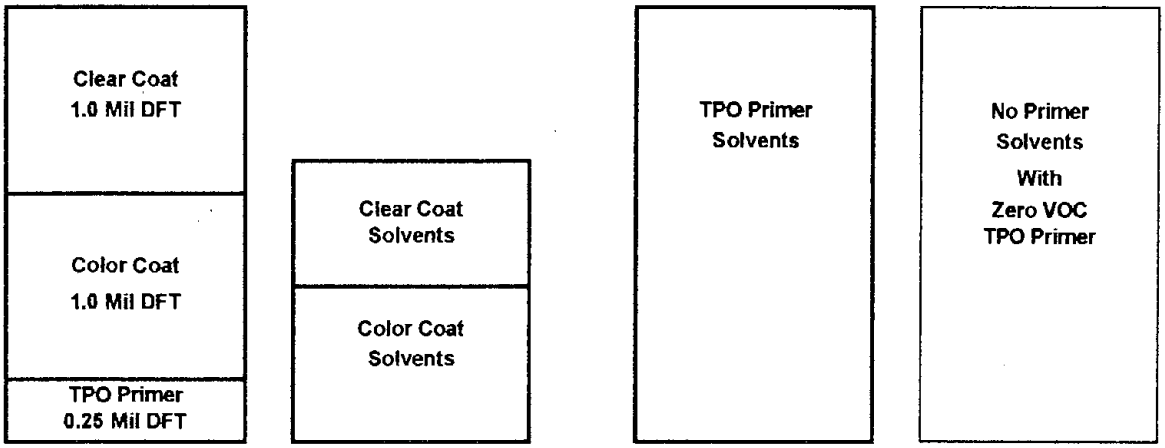
Automotive exterior color coats notwithstanding, there are other applications of great interest in the automotive industry for compliant materials which have resulted from this extensive evaluation of technology. Remaining for the moment on applications for metal substrates, a compliance material has been developed in a zero VOC water-borne material for use as a transit coating for protecting the exterior of the automotive or light truck surface during storage and shipment. Applied as a water-borne solution coating, the material dries to a water-resistant film which while in place is equally resistant to acids (acid rain, airborne contaminants, etc.), and upon arrival at the dealer, is removed in conjunction with the use of an alkaline cleaner solution which is sprayed onto the surface, allowed to remain in contact with the surface for a couple of minutes, and then removed with a pressurized water rinse. Use of a material of this sort is a consideration both as an additional protection for high-end models where every measure of surface enhancement is being taken, and in replacement of the contact film laminates currently in vogue for this sort of protection. The films, while functionally effective, are relatively expensive (typically above $10.00 per vehicle), can be difficult to remove, and create a disposal issue for the dealer which is an additional hurdle. The water-borne solution, while essentially clear, can be dyed slightly (if desired) to be more evident once in use.

Staying with the automotive market, but moving into the growing arena in the use of plastics, an application which has generated extensive VOC levels (and in so doing has limited its development despite considerable customer interest) has been the painting of polypropylene and other olefinic substrates. These materials are of great interest in the automotive market in that they are relatively inexpensive, are completely recyclable into themselves (primary surface uses

can be ground up and re-used as a primary surface, not relegated to backers and other non-critical uses due to an inability to provide a smooth surface), and they exhibit good weathering characteristics in their own right. The weakness of these materials relates to the difficulty of obtaining the required adhesion of paints and adhesives on these surfaces. As a result, these materials have typically required an adhesion promoter prior to the application of the color coat. These coatings, typically applied in very thin (0.1-0.2 mils DFT) films, have traditionally been very low solids products (5-6% volume solids is not unusual) containing an associated high level of aggressive coalescent solvents, designed to penetrate the surface of the plastic and to set up adhesion sites for the subsequently applied color coats. It is not unusual for the solvent-borne materials of this type to generate 6.0-7.0 pounds per gallon of VOC's,

CHART SEVEN: Zero VOC TPO Finishing Process

Comparative	Solvent	Volumes
Solvent Clear Coat		60% Volume Solids
Solvent Color Coat		50% Volume Solids
Solvent TPO Primer		10% Volume Solids



which can effectively offset any compliance of the subsequent topcoats because of the very high volume of VOC's released in their application. This impact is demonstrated on the attached chart. As you can see, in an operation coating 100,000 square feet of material at 0.2 mils dry film thickness with equipment providing 70% transfer efficiency, more than a ton of VOC's could eliminated per year in the use of a zero VOC adhesion promoter versus a more traditional material. Development work undertaken to provide a material of this sort has resulted in a patented zero VOC waterborne emulsion-type material. This product is applied in equally thin films from a much higher solids material (13% volume solids).

Optimum film formation with this material occurs in the presence of heat, as it requires an exposure to 180F. at some point during the process cycle. Interestingly, this exposure to heat can come during the curing of the subsequently applied topcoat, allowing the adhesion promoter and topcoat to be handled in a wet-on-wet application process if there is no existing provision for curing the adhesion promoter by itself. This in no way reduces the properties of the adhesion promoter or the subsequently topcoated material. Once the adhesion promoter and topcoat are in place, they perform very well in the most aggressive automotive evaluations, including thermal shock and other deployment analysis, which are sufficiently destructive to expose a film weakness

very quickly. In those applications which are not topcoated, but rather are intended for the bonding of an adhered companion surface (typically the double-sided tape used to bond body-side moldings, etc.), this material serves as an excellent foundation for the existing adhesives to allow the olefins to compete for these applications which have previously been dominated by the use of PVC. The strength of PVC has been in its superior adhesion, while the weaknesses of PVC have

CHART EIGHT: Zero VOC TPO Primer Description

Weight Per Gallon	8.55 Pounds
Weight Solids	15%
Volume Solids	13%
Recommended Film Thickness	0.2 - 0.4 Mils DFT
Theoretical Coverage @ 0.2 Mils DFT	1043 Sq. Ft./Gallon
Package Viscosity	200 - 400 cps (Brookfield)
Thinner (If Desired)	Tap Water
pH	8.5-9.5
Flash Point	None Measurable
VOC's (Pounds Per Gallon)	Zero

been in exterior weathering (to the point of requiring a clear coat) and in its non-recyclability into an equivalent use. Once the issues relating to the adhesion of the tape to an olefin are resolved, however, with a material of this sort many other design options open up for the end user. In addition to this material being provided in a standard clear formulation, it is also available in a pigmented conductive version, intended to enhance the electrostatic properties of the substrate for subsequent application of color coats. This can be a significant benefit for first pass transfer efficiency on molded or intricately shaped parts, and as such, can provide additional economic incentives to consider a material of this sort.

[It should be stated once again that the chemistry of the adhesion promoter is completely different from any of the other low and no VOC materials discussed in this paper.]

Summary

The issues related to the implementation of these various technologies will vary by region, by industry and by facility. It is becoming clear that the Clean Air Act will be enforced with varying emphasis from region to region, and it is too early to tell whether the tenets of the regulations which call for uniform enforcement across similar industries will materialize. Eventually, however, there can be little doubt that the intentions of the Clean Air Act and its Amendments will be

enforced, and that there will be little forgiveness for having ignored its requirements. It is unrealistic to imagine that the conventional high solids (60% or so volume solids) materials in wide-spread use today will meet the requirements of the regulators without the installation of extensive control equipment. For this reason, it is equally unlikely that the liquid coatings manufacturers will spend any measurable portion of their development budgets in the future on making a "better" 60% solids material. Selective development investments in water-borne systems will certainly continue, particularly in the zero VOC water-containing materials where a real contribution can be made to lowering emissions. It will be unlikely that similar levels of investment in product development will be undertaken on a wide-spread basis in powder coatings for some fundamental reasons. There is sizable over-capacity in the North American powder coatings market currently, with over 60 manufacturers of most chemistries. The result of this combination, not surprisingly, is an ongoing commoditization of the powder coatings market as prices are driven down to a level which makes it difficult to justify true product development activities. In addition, there are so few powder coatings manufacturers who are basic in resin manufacture that the bulk of the market is left to pick materials from a common raw material base in which differentiation is almost impossible. There will always be a market for powder coatings, certainly, but the "easy" improvements in this technology have already been realized. The more difficult hurdles confronting powder coatings (mentioned previously) will not readily disappear, and the availability of a viable liquid material which effectively removes these hurdles changes the issues when an end user confronts his options for equipment conversion and process compliance.

The core message of this presentation is quite simply this: for the broad-based requirements of the general industrial coatings marketplace (office furniture-files-partitions, appliances, shelving, tool boxes, commercial and residential metal furniture, electrical component enclosures, and other general metals end uses), liquid materials are available TODAY which provide the optimum blend of performance and compliance, coupled with value economics which allow the end user to achieve all of his needs.

ALTERNATIVE DIELECTRIC COATING MEDIUM FOR ELECTRIC MOTOR FIELD COIL MANUFACTURE

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INTRODUCTION

A combination of company policy to reduce use of 33/50 chemicals, increasing production rates and implementation of the Clean Air Act Amendments (CAAA) with regard to emission limits of hazardous air pollutants (HAP) led General Electric (GE) Small Motors-Dothan to initiate a project with The University of Alabama to find a satisfactory solution to the potential problem of excess xylene air emissions from varnish curing operations. The process of interest was the coating and curing of small motor field coils with a polyester varnish using xylene as the carrier. Replacement of the current varnish with a waterborne varnish would help the plant meet environmental regulations while still expanding to take advantage of higher productivity potential in the plant. An additional benefit expected was a potential energy savings. The project was funded by the Alabama Universities-Tennessee Valley Authority Research Consortium (AUTRC) and GE, with cost-sharing by the University. GE and the University of Alabama had worked together previously on a waste reduction project in an epoxy armature-coating operation with satisfactory results.

BACKGROUND

The General Electric Company's Dothan Motor Plant produces 20,000 motors per year in a size range of 1-60 HP. The plant began production in 1975, and employs 300. In order to improve productivity and competitiveness, all manufacturing processes are being reviewed with a view towards minimizing or eliminating hazardous or other wastes and by-products while reducing costs and processing time.

Field coils are a component of motors, and the coating process for this item is under study by GE as a target for improvement. A polyester varnish coating is applied to the formed wires to stabilize the configuration and to protect the current-carrying wires in the field coil. Characteristics required in a good varnish in this application are dielectric strength, bond strength, and good thermal stability. The coating process includes coating application, forming, and convection oven curing for a total of 1.5 hours, after which the field coil enters the next manufacturing step.

Problems with the current process include energy usage, process time, safety and environmental concerns from the solvents contained in the varnish, varnish residue, and waste disposal.

ORGANIZATION

The GE plant is organized around a total quality management concept, the organization is essentially one-tiered, and the contact for the project was the quality business team leader. This organization allowed for excellent communication and action, and GE personnel reflected an open-mindedness and cooperation which helped the project move ahead. In addition, there was experience from an earlier project which eased orientation and personnel relationships. The University effort was accomplished by a research engineer and a graduate student, with oversight by Chemical Engineering faculty. The waterborne varnish supplier provided ample samples, field test equipment, extensive laboratory testing facilities, and personnel for field trials.

METHODS

A review was made of the existing production processes for coating and curing field coils using a xylene solvent polyester varnish at 50% solids. The main focus was on one of three lines used to produce field coils in the plant. Coils in this process are wound, pre-formed, dipped and cured, cooled, taped, re-dipped and cured, partially cooled, formed, and cooled. A family of waterborne varnishes was selected after discussion with GE's technical support staff, who had been reviewing candidate varnishes. These varnishes feature no or low VOC content, and a possibly shorter time and lower temperature cure cycle. Facilities were prepared for batch dipping and curing of coils. Tests were done with these varnishes in the laboratory for physical characteristics and in batch coating of coils for cure optimums, and in side-dip plant trials to determine efficacy. Final recommendations were made to GE Small Motors Management.

Existing Production Processes

Three areas of field coil production were identified, the Lanly oven/industrial main coil area, the Michigan oven/BT coil area, and the Dispatch oven/SMR field wound area. GE personnel suggested that the Lanly /industrial main coil area is the prime process area for this project, since the process can be easily duplicated in laboratory-scale tests, as the coils are separate and easy to manipulate. In this process, the prepared wound and preformed coils are hung on a conveyor which passes the coil through a bath, containing the current varnish and into an oven cure at 350°F for 90 minutes. Xylene is added to the varnish to control viscosity. Natural gas is the energy source for all three ovens. The coil then receives a nylon and fiberglass tape cover and is treated again in the same way, partially cooled, re-formed, cooled and installed in the motor frame after testing for insulation integrity. Chemical components are provided from the storeroom in five gallon pails. A waste drum, labelled hazardous, contained drippings obtained during routine cleaning and oven clean-out, which is done every week. The bath is kept at ambient temperature and the viscosity and level are checked on a routine basis. Venting of fumes to roof or side-wall

is accomplished with vacuum hoods and fans.

Evaluation of Alternative Coatings

Two alternative coating materials were already selected by GE for testing. Evaluation of the varnish physical properties were critical for the success of this project. Dielectric strength is more important with this coating than the bond strength and adhesion in the armature/epoxy system studied last year, since the coil is relatively static. However, vibration can be a problem, so the final cure must be such that the coating retains integrity under thermal stress found in DC motors. Testing for physical properties and comparison to the existing varnish was carried out at the supplier's laboratory in the presence of the University project team members. This laboratory was well equipped with specialized equipment for complete testing of varnish coatings using accepted ASTM methods.

Routine physical property measurements of the varnish such as solids content and viscosity was carried out in the University's laboratory using standard procedures recommended by the supplier for solids content and GE's preferred viscosity testing using a Zahn viscometer. Bulk curing tests were attempted in aluminum cups. Measuring the hardness of the varnish cure was attempted using a penetrometer. Batch coating and curing of test coils with the new varnishes was accomplished at the University's Chemical Engineering facilities with equipment specially built for this project. Un-coated coils were supplied by GE, and varnish by the supplier. Trials were made to establish the level of coating retention, and to determine time and temperature parameters for an acceptable cure of the coil. Visual determination of coating thickness, uniformity, and completeness within the coil was attempted by electronic microscope techniques. Also, the hardness of the coil coating was estimated from penetrometer data.

Side-Dip Plant Trials

Successful laboratory tests were confirmed in side-dip plant trials. Using approximations to existing processing conditions on the Lanly Oven line, for example, coils were treated with the proposed varnish by dipping into a pail of the varnish and then putting the coils into the production line just after the normal varnish dip. In several tests, a DATAPAQ recorder (DATAPAQ, Inc., Wilmington, MA) was attached to a treatment coil allowing temperature measurement of air, coil surface, and coil interior throughout the curing cycle. Trials were also attempted on the Michigan Oven line. A DATAPAQ recorder was again utilized, but testing of the coils subsequent to curing was limited to electrical integrity only, which was acceptable, due to the fact that the coils are already mounted in housings.

RESULTS

Physical Property Tests

The initial proposed water-borne varnish selected was designated as P.D. George (PDG) 1000-Low VOC Waterborne Insulating Varnish (P.D. George Company, St. Louis, MO). Limited physical property testing for solids content (specified at 30%) and viscosity indicated variations from specification. P.D. George indicated that these problems were due to weather-related manufacturing situations, which were subsequently cleared up. Later in the project, this product was offered and tested at 34% solids, in an attempt to improve film build characteristics. Lastly, a product with slightly higher VOC content, designated as 1000-70B, with 70% solids was tested in dilutions down to 35%.

Major physical property testing of 1000-Low VOC in comparison with GE's existing xylene-based varnish was done at the supplier's laboratory facilities in St. Louis on June 13, 1994. Basically, the waterborne varnish was as good or better in tests such as dielectric strength, helical coil bond strength, pencil hardness, flexibility, and surface and volume resistivity. Film build was significantly less for the proposed varnish, which was of concern to GE.

Tests were done in the University's laboratory on the xylene-based varnish currently used by GE and the new water-based formulations for viscosity. Results are given in Table 1. Bulk testing for optimum cure cycles was attempted with poor results due to bubbling. However, samples of the current xylene-containing varnish were cured at different temperatures and subjected to a modified penetrometer test to measure degree of hardness. Conventional hardness testing equipment such as Rockwell, Brinell, and Vicker could not be used as the samples were too soft. Samples cured at 130° & 150°C were too soft to achieve results, but the data obtained for 170° and 190°C confirm an increase in hardness at higher temperatures.

The wire from a field coil was coated with both varnishes and cured and thickness measured with a micrometer. The xylene-based coating was thicker on average (two thousandths vs one thousandth). The coated wire was bent at a sharp angle and viewed under an optical microscope with polarized light at magnifications from X50 to X200. No distortion or fracture of the coating wall was observed.

Coated coils from both treatments were cross-sectioned for microscopic analysis. It was observed that the xylene-based varnish-treated coil was more compact than the water-based varnish-treated coil. Also, the xylene-base coating showed more uniformity of coating between the individual wires than did the water-base coating.

Laboratory Coating and Curing Trials

Table 2 summarizes significant results from coating and curing trials in our laboratory during the project. Parameters for varnish treatment of the field coils under

Table 1

Viscosity of Current and Proposed Varnishes

Zahn Viscometer seconds at 24°C

	XYLENE BASE	1000 - 70B	1000 - LOW VOC	1000 - LOW VOC	WATER
% SOLIDS	50	35	34	30	0
ZAHN CUP #1	188-191	133-135	50-51	32-33	30-31
ZAHN CUP #2	94-96	65-67	23-25	16-17	15-16
ZAHN CUP #3	46-48	32-34	11-12	7-8	7-8

Table 2

Summary of Coil Curing Laboratory Trials

VARNISH: IMI 9637. XYLENE BASED SOLIDS CONTENT: 50%				
SOLIDS,%	CURING TEMP., C	CURING TIME, MIN.	VARNISH USED, g	REMARKS
50	177	90	20.3	Currently in use in GE Dothan Plant

VARNISH: 1000 LOW VOC WATERBORNE SOLIDS CONTENT: 30%				
SOLIDS, %	CURING TEMP., C	CURING TIME, MIN.	VARNISH USED, g	REMARKS
30	150	60	8.2	a. First cure: very hard b. Second cure after wrapping: hard c. Film buildup: poor
30	140	60	9.0	a. First cure: medium hard b. Second cure: hard; B staging: not good c. Film buildup: poor

VARNISH: 1000 LOW VOC WATERBORNE SOLIDS CONTENT: 34%				
SOLIDS, %	CURING TEMP., C	CURING TIME, MIN.	VARNISH USED, g	REMARKS
34	121	60	13.8	a. First cure: very soft b. Not done c. Film buildup: poor
34	140	60	12.7	a. First cure: medium hard b. Second cure: very soft, pressing not effective c. Film buildup: poor
34	140	90	13.3	a. First cure: hard b. Second cure: good c. Film buildup: poor

Table 2 (Continued)

Summary of Coil Curing Laboratory Trials

VARNISH: P ED 1000 - 70B SOLIDS CONTENTS: 70%			WATERBORNE DILUTED TO DIFFERENT PERCENTAGES	
SOLIDS,%	CURING TEMP., oC	CURING TIME, MIN.	VARNISH USED, g	REMARKS
50	150	70	20.1	a. First cure; very hard b. B-staging: no c. Film buildup: thick, as good as xylene varnish
40	150	75	19.2	a. First cure: very hard b. B-staging: no c. Film buildup: excellent
40	150	70	19.0	a. First cure: very hard b. B-staging: no c. Film buildup: excellent
40	150	60	18.3	a. First cure: medium hard b. B-staging: not satisfactory c. Film buildup: good
40	150	45	19.1	a. First cure: soft b. B-staging: very soft c. Film buildup: excellent
35	160	60	17.3	a. First cure: hard b. Second cure after wrapping: soft c. Film buildup: good
35	150	60	17.0	a. First cure: soft b. B-staging: no c. Film buildup: good
35	135	50	18.8	a. First cure: soft b. B-staging: no c. Film buildup: good
35	121	40	20.0	a. First cure: very soft b. B-staging: no c. Film buildup: excellent
35	110	90	17.2	a. First cure: very soft b. Second cure: very soft c. Film buildup: good
35	125	90	19.2	a. First cure: medium hard b. Second cure: soft c. Film buildup: excellent
35	140	90	19.0	a. First cure: hard b. Second cure: fair c. Film buildup:excellent
35	150	90	18.9	a. First cure: hard b. Second cure: good c. Film buildup: excellent

the current operating conditions in the GE plant are given. Coils are dipped in a 50% solids varnish containing xylene as the solvent, and are cured at 177°C for 90 minutes. Varnish retention on the coils was 20.3 grams.

Data is also given on the tests done using the PDG 1000-Low VOC waterborne varnish at 30% solids. Using the reduced curing temperature of 150°C and reduced curing time of 60 minutes as recommended by PDG, the cure was very hard, but it was found that the cure softened on reheating. Also, the varnish retention of only 8.2 grams is significantly less than the current standard, indicating insufficient film build. A rerun of this material using a curing temperature of 140°C gave a slightly softer cure. Again, the varnish retention is only 9 grams.

Tests with the 1000-Low VOC material with the solids content raised to 34% are also presented. This material was supplied by PDG after the low retention results in our lab trials and in a side-dip plant test. The results of the laboratory tests are slightly better than the 30% solids data, but still are short of the targeted retention of about 20 grams found in the control, currently used product.

Lastly, tests with PDG's 1000-70B, a 70% solids material with somewhat higher, but still acceptable, VOC content are also given. The material was diluted to a range of 35-50% solids. Curing temperatures tested ranged from 110°C to 150°C with curing times from 40 to 90 minutes, the latter time being the current standard operating time in the plant. From the results of these trials, it appears that this material, diluted for economy sake to 35% solids, retains enough viscosity to give a retention similar to that of the control xylene varnish (Table 1), and cures well at a lower temperature of 140-150°C.

Side-Dip Plant Trials

Side-dip plant trials were done on June 6 and November 30, 1994, with University and supplier personnel present.

On June 6, trials were done on both the Lanley and Michigan Oven lines, using 1000-Low VOC material at 30% solids. Six coils were treated in the Lanley Oven with the test material and were subsequently distributed three each to the University and to PDG. The DATAPAQ data collector was utilized to collect temperature and time through the oven. Lanley coils were checked for cure visually and appeared almost overcured when reformed. When cut in cross section, the lack of film build was apparent and the wires were not firmly bound in a cohesive matrix. A test was also done on the Michigan Oven line with two coils, and the DATAPAQ was again utilized, but no results could be drawn from the test due to the difficulty in evaluating the Michigan coils which are already mounted in motor housings.

Trials in November were accomplished on both lines using both 1000-Low VOC at 34% solids and 1000-70B High Solids diluted to 35% solids. The Lanley coils were

deemed satisfactory using 1000-70B High Solids material diluted to 35% solids and cured at 163°C for 90 minutes. The Michigan coils are still being evaluated at the time of preparation of this report by GE and PDG, using a humidity test procedure to confirm proper coating of the NOMEX paper in the motor mount.

DISCUSSION

Tests with proposed waterborne varnishes indicate that they perform well compared to existing xylene-containing varnishes. However, in this project, problems were encountered with quality control of solids content. Apparently, supplying companies are not experienced in the problems relating to storage and shipping of water-containing formulations during winter months. Care must be exercised in acceptance of these materials in cold weather periods.

Viscosity variations from solvent-based materials to waterborne materials will also require attention. In this case, the recommended varnish at 30% solids was close to the viscosity of water, and retention of the material on a multi-wire coil of up to 1.5 inches diameter after a short ambient temperature dip was not sufficient. These results led to the supplier offering a variation up to 34% solids, but the increase was not enough to significantly improve the retention rate, as the viscosity was still significantly lower than the current varnish mix.

The supplier indicates that the solids content of 1000-Low VOC cannot be further increased. This material contains no co-solvent, only a pH adjusting chemical, dimethylethanol amine (DMEA), and has less than one pound of VOC's per gallon.

Alternatively, 1000-70B High Solids Water Borne Insulating Varnish at 70% solids and 2.63 pounds of VOC's per gallon was diluted to 35% solids and gave a satisfactory viscosity and coating retention. Use of this product would result in significantly less VOC's (2.63/2) than the existing xylene-based varnish (about 3.85 pounds per gallon VOC's), a reduction of 65%.

Potential energy savings also exist with the waterborne coatings. The supplier has indicated a curing temperature as low as 121°C for 60 minutes would give a satisfactory cure, while our tests indicate that 140-150°C are required. This is still significantly below the existing 177°C - 90 minutes condition in the Lanly Oven line.

Considering the current state of xylene emissions at the plant and anticipated production increases, a move to the 1000-70B High Solids waterborne material diluted to 35% solids appears to be a viable alternative for the GE plant for the Lanley Oven line. The data collected should also apply to the Michigan Oven and Dispatch Oven operations, but no concrete data has been collected in this study for confirmation.

CONCLUSION AND RECOMMENDATIONS

Based on the results of laboratory physical properties testing, laboratory coating and curing trials on prototype coils, and side-dip plant testing, carried out in the University's laboratories, the supplier's laboratories, and at the GE plant, replacement waterborne low VOC varnishes represent a viable alternative to xylene and other high VOC-containing insulating varnishes in field coil coating operations. Replacement of these varnishes will meet a corporate goal at GE for VOC reduction, will help the plant minimize adverse effects of the Clean Air Act Amendments (CAAA), reduce emissions reported on SARA Title III Section 313, reduce hazardous wastes, improve worker health and safety, and reduce energy consumption. GE management at the Dothan Motor Plant agree with this conclusion and expect to replace the xylene-containing varnish with the waterborne varnish as soon as practically possible, probably by mid-1995.

The results from this study can most probably be applied to other similar varnish coating manufacturing, including motor rebuilding shops.

ACKNOWLEDGEMENTS

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Odour and VOC emissions reduction on coil-coating lines by using waterborne paints - part. II: full waterborne system application

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1. Foreword

It is more and more admitted that the use of abatement techniques in order to reduce Volatile Organic Compounds emissions will not allow to achieve in the future the planned rejection objectives. This fact is especially admitted; indeed the abatement techniques located at "end of line" will always have a limited efficiency while their investment costs, possibly operating costs, can penalize products competitiveness.

Therefore, chemical industry agreed to make particular efforts for the elaboration of substitution products in order to eliminate as much as possible the organic phase. By suppressing the emission source, nuisances, which can affect workers as well as the environment, are eliminated.

In particular, in the paints field, new types of systems have appeared : paints formulations, coating application mode, etc...

Unfortunately, the originality of the proposed systems usually requires a deep process readjustement since the required application or curing mode is totally different. Finally, these systems are not yet adapted to all materials, for instance the application processes based on U-V or electron beam curing for steel [1]. For the chosen example, i.e. coil-coating where paint is applied on a steel sheet running continuously through roll coaters, homogeneity and layer thicknesses are typical characteristics of the delivered product. In this industry, only a few paints, which can be considered as high solids, are used (e.g. PVC), as well as waterborne paints chosen as primer or backer.

The present paper presents the advancement of an E.C. research [2] studying the feasibility of waterborne systems for coil-coating applications. Nowadays in Europe almost coil-coaters are using exclusively Organic Based Solvent (OBS-) paints. The SOLLAC steelmaker group, especially on its industrial plant localized at Onnaing (France), is an exception: great interest is accorded to Waterborne (W-) systems because their use allows to increase the rate of production without explosive problems. So, W-paints are used as backer.

After some generalities giving informations about the coil-coating process and the analytical methods which were used, the paper will be divided into three parts:

- comparison of two epoxies (OBS- and W-) used in a semi-classic paint system (OBS-primer and OBS-top coat + W-backer);
- presentation of the test results from a full waterborne system at industrial scale;
- comparison of the W-system with a full OBS-system.

All results are presented on the basis of equivalent ESP's* .

2. Generalities

2.1. Description of the coil-coating line

The concept of a coil-coating line is shown in figure 1.
Steel and galvanized steel coils 600 to 1500 mm wide and 1,25 to 1,5 mm thick are alternatively unrolled on two drive machines; a stitching machine realizes the junction between rolls and ensures a continuous steel sheet at the inlet of the installation. The accumulator allows to feed the "process" section during these stitching operations.
A surface treatment is carried out in order to provide, in addition to the anti-corrosion properties, an excellent adhesion of paints on the metal.
The sheet arrives then in the paint cabin (more or less 300 m^3 volume). A first machine, equipped with rolls, allows to apply :
- on the upper side: a 5 µm thickness dry primer;
- on the lower side: a 7 µm thickness dry backer.

After passing in the primer oven (20 s to 1 min according to the speed), a second layer is deposited by a second painting machine (10-19 µm top coat giving the color and the organic coating characteristics) before entering in a second oven (finish oven) and undergoing a cooling under water before rewinding of the coil after the checking post.

Each oven is followed by a dedicated thermal incinerator. The incinerators are supplied by extractors which keep the ovens depressurized.
Thanks to a gas input, the combustion of organic solvents contained in the paints takes place at about 700°C and allows for cracking these solvents.

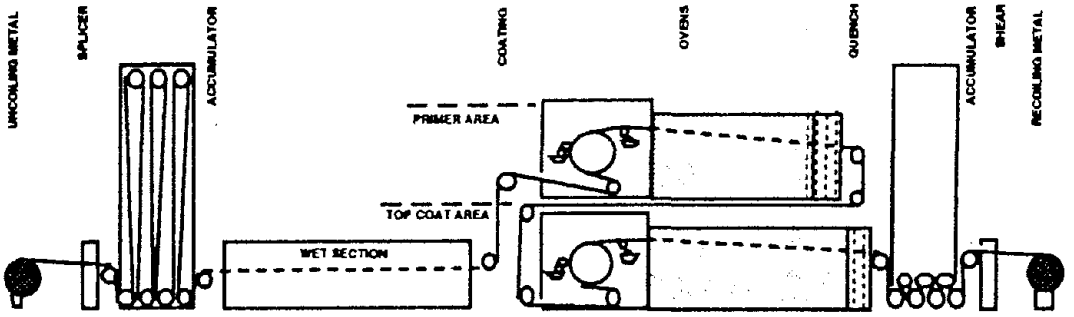

Fig. 1 - Diagram of a coil-coating line

2.2. Analytical methods

The given results in this paper concern odour levels measurements coupled with high sensitive chemical analysis; the odorous power (pOU) is a tool used as intermediate result to link chemical compounds concentration with odours concentration.

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* ESP: dry content of the paint, % volume

Odours are measured by means of an dynamic olfactometer (ODILE from Société Belge de Filtration) in reference to the latest works of the European Committee of Standardisation (CEN) [3]. Z is the dilution factor expressed as $\frac{Q+Qod}{Q}$ and r/p is the ratio of perception positive responses of the panel (r) on the full number of presentations of a dilution (p) (number of panellist x number of individual presentation) (see figure 2). The odour concentration (Z_{50}) is determined as occuring to the more probable dilution by the PROBIT [4] statistic at the level (1- α) matching 0,95. Q and Qod are respectively the inodor air and the odorous sampling flow-rates delivered by the olfactometer. This measure is independent of the odour quality.

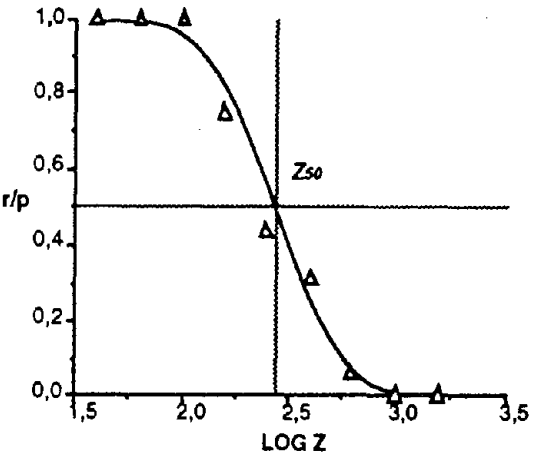


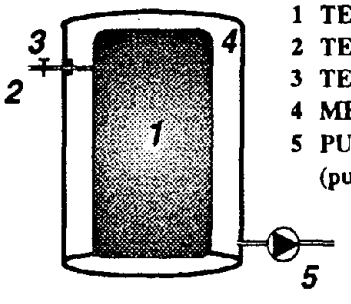
Fig. 2 - Example of an odour curve plotting and odour concentration determination: (△) Experimental response of the panel (positive perception); (–) Statistic fitting for Z_{50} determination (PROBIT): Z_{50} = 274 u.o./m^3

The above procedure is useful to determine the odours annoyance and allows for comparing levels of odours concentrations. It is important to determine which compound or group of compounds is responsible for the odour annoyance. This information can only be obtained by means of high sensitive chemical analysis like chromatography coupled with mass spectrometry (GC-MS).
Correlations can be made in such a way between the air sample analyzed and the applyed paint. So, paint analysis are made in order to determine which compounds are emitted during application by means of dynamic headspaces through the paint.

The pOU illustrates the individual contribution of each volatile compounds identified in the perceived odour. Following its definition it is expressed in term of odour decibel (dBo) as

$$\Sigma\, pOU_i = \Sigma \log(\frac{C_i}{d_i}) \qquad [dBo]$$

where C_i and d_i are respectively the detected concentration of the volatile compound and its individual odour perception threshold (pOU = 0 when $C \leq d$).



1 TEDLAR BAG
2 TEFLON TUBE
3 TEFLON VALVE
4 METAL DRUM
5 PUMPING SYSTEM
(pump, battery, flexible tube, flowmeter)

Fig. 3 - Vacuum sampler

Sampling is made via TEDLAR bags which give, with a minimum of precautions, accurate results. Bags are filled as much as possible by a direct vacuum system shown at figure 3.

Both samples for olfactometry or for chemical analysis are made this way. For chemical analysis, several milliliters of gas are passed through an adsorbent cartridge before to be put into a Thermal Cryogenic Trap (TCT) system as injection device into the GC-MS. Quantification is made in reference to standards. Detection limit of the system is in the range of 0,01 - 0,1 ppb (or $\mu g/m^3$).

2.3. *Paint composition*

Solvent phase compositions for equivalent organic/water paint systems are given in the table I (from PPG [5]).

Table I - Comparison of paint compositions for equivalent organic/water systems

Paint	ESP %	Coverage $\mu.m^2/kg$	SOLVENT COMPOSITION (% Vol) aromatics	alcohols	esters	ketones	water
PRIMERS							
OBS-Epoxy	51	310	64	30	-	6	-
W-A-Epoxy	43	310	-	29	7	-	64
TOP COATS							
OBS-P E	63	350	59	24	17	-	-
W-Acrylic	60	350	-	27	-	-	73
BACKERS							
OBS-Epoxy	50	320	52	29	10	9	-
W-A-Epoxy	49	310	-	32	-	9	59

	Compounds	Bulk %
1	Isobutanol	0,36
2	n-Butanol	2,67
3	Benzene	8,55E-04
4	2-Butanone	0,4
5	Ethyl glycol acetate	0,01
6	1-Methoxy 2-Propanol	3,86
7	Toluene	7,65
8	3-Hexene-2-one	0,4
9	Cyclohexanone	0,76
10	4-Methyl 2-Pentanone	0,12
11	Σ C7 alkanes (Heptane incl.)	1,75E-03
12	Ethylbenzene	3,67
13	m+p-Xylenes	5,97
14	o-Xylene	2,37
15	5-Methyl 2-Hexanone	1,19
16	Σ C8 alkanes	2,18E-03
17	Indene	0,02
18	4-Methyl 4-Hydroxy 2-Pentanone	4,7
19	Isobutyl acetate	0,03
20	Butyl acetate	0,5
21	Methyl styrene	0,67
22	2-Butoxy ethanol	0,1
23	Methyl Cellosolve acetate	2,12
24	Σ C3 Alkylbenzenes (=)	0,48
25	Σ C3 Alkylbenzenes	31,11
26	Naphtalene	0,3
27	Σ C9 alkanes	0,09
28	1-Methyl 2,3-Dihydroindene	4,51E-03
29	Cellosolve acetate	-
30	Σ C4 Alkylbenzenes (=)	0,54
31	Σ C4 Alkylbenzenes	21,36
32	Isophorone	0,73
33	Σ C10 alkanes (Decane incl.)	0,39
34	Ethylene Glycol diacetate	0,47
35	Σ C5 Alkylbenzenes	1,46
36	Σ C11 alkanes	0,07
37	2-(2-Butoxyethoxy) ethanol	0,09
38	Butyl diglycol acetate	0,3
39	Ring ether	3,8
	SOLVESSO/SHELLSOL	55,27

As illustrated by tables II and III, the composition of OBS-paints can be complex because of the great use of petroleum cuts (Solvesso/Shellsol) as solvent. The choice of the organic solvents is more functional for W-paint.

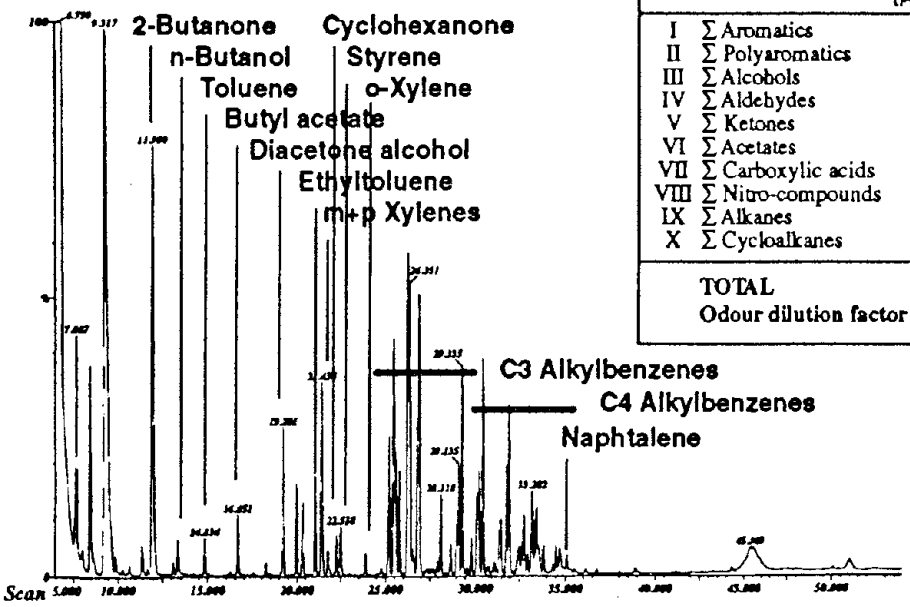
COMPOUNDS	Bulk (%)
Butyl Glycol	25
n-Butanol	23
Toluene	16
Methyl Pirrolidinone	14
Butoxyethoxy ethanol	14
Amines and surfactants	9

Table II - Typical organic solvent content of a W-paint

Table III - Compilation of solvent phase content for based organic solvent paints [6]

3. Comparison of paint cabin ambiences

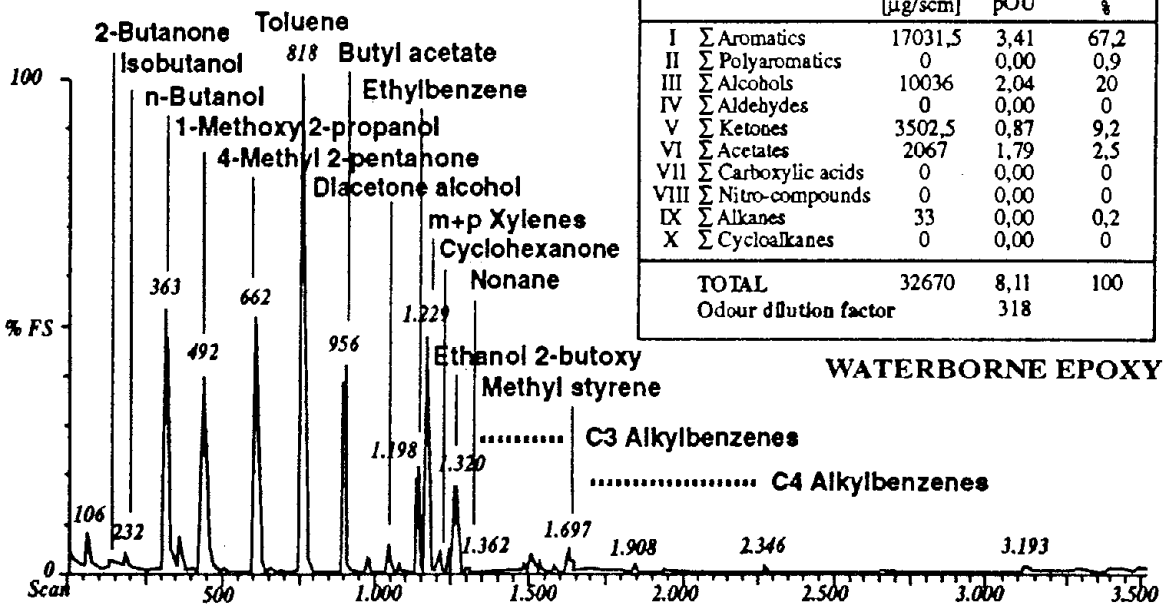
This section compares the emissions occuring during the primer (or backer) coat application of an OBS-epoxy and a waterborne one. Analysis for the W-epoxy was made during the application of a "semi-classic" paint system (primer and top coats being OBS and backer being a W-paint).



	SPECIES	WORK PLACE [µg/scm]	pOU	PAINT %
I	Σ Aromatics	29793	4,17	78,88
II	Σ Polyaromatics	465	0,97	0,06
III	Σ Alcohols	3142	0,89	1,90
IV	Σ Aldehydes	-	-	-
V	Σ Ketones	4581	0,29	9,99
VI	Σ Acetates	1704	0,89	9,16
VII	Σ Carboxylic acids	34	0,14	0,02
VIII	Σ Nitro-compounds	-	-	-
IX	Σ Alkanes	-	-	-
X	Σ Cycloalkanes	-	-	-
	TOTAL	39718	7,36	100,00
	Odour dilution factor		382	

EPOXY

Fig. 4 - Chromatogram of a work ambience during the application of a OBS-EPOXY as primer coat (recapitulative table of quantitative results in locket)



	SPECIES	WORK PLACE [µg/scm]	pOU	PAINT %
I	Σ Aromatics	17031,5	3,41	67,2
II	Σ Polyaromatics	0	0,00	0,9
III	Σ Alcohols	10036	2,04	20
IV	Σ Aldehydes	0	0,00	0
V	Σ Ketones	3502,5	0,87	9,2
VI	Σ Acetates	2067	1,79	2,5
VII	Σ Carboxylic acids	0	0,00	0
VIII	Σ Nitro-compounds	0	0,00	0
IX	Σ Alkanes	33	0,00	0,2
X	Σ Cycloalkanes	0	0,00	0
	TOTAL	32670	8,11	100
	Odour dilution factor		318	

WATERBORNE EPOXY

Fig. 5 - Chromatogram of a work ambience during the application of a W-EPOXY as primer coat (recapitulative table of quantitative results in locket)

Measurements were lead into two different coating plants; the air dilution flow-rate around the paint machine corresponding to the figure 1 (OBS-epoxy) was exactly the double of the flow-rate value corresponding to figure 2 (W-epoxy). So it can be seen

that the same levels of concentration and odours are reached when using the waterborne paint although the air dilution flow-rate was reduced by a factor 2.
The chromatograms reflect very well the differences between the two systems. It can be pointed out that the overall composition of W-paints is in accordance with the formulation given by the manufacturer only from a qualitative point of view.

On the basis of those results it was decided to begin an ECSC research to study [2] the application of a full waterbone system.

4. Full waterborne system

4.1. Results of measurements

Trials were led on the site of Onnaing (France) with a system constituted of three coats (primer, backer and top coat). Primer and backer are waterborne epoxies whereas top coat was an acrylic one. Table IV summarizes the obtained results on the three work place areas whereas the Table V summarizes the obtained results on both sides of the two incinerators (inlet and outlet).

The chromatogram at figure 6 shows the GC-MS analysis on the inlet effluent of the incinerator treating emissions from ovens drying and curing backer and top coats (respectively, chromatograms shown at fig. 7 and 8).
The chromatogram (figure 8) obtained for the analysis of the top coat paint (waterborne acrylic) can be compared with the chromatogram (figure 9) obtained for the analysis of a based organic solvent paint (polyester).

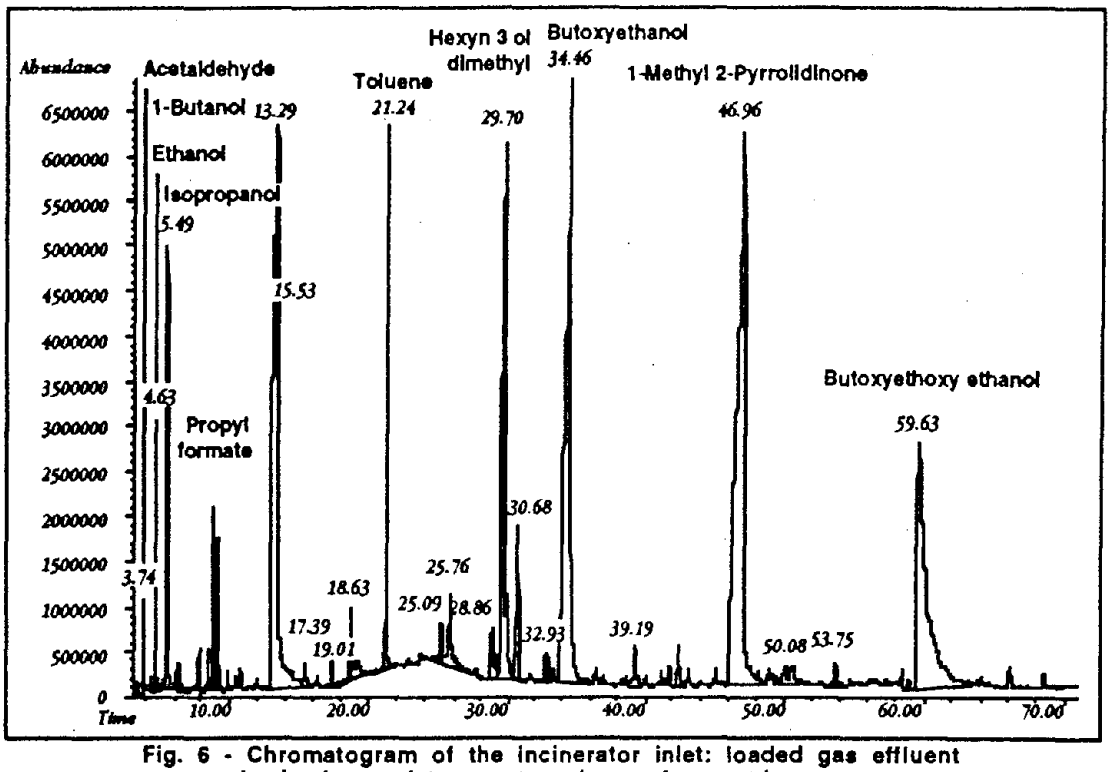


Fig. 6 - Chromatogram of the incinerator inlet: loaded gas effluent by backer and top coats solvents from curing oven

SPECIES	BACKER				TOP COAT				PRIMER			
	Work place			Paint	Work place			Paint	Work place			Paint
	[µg/m 3]	Σ pOU	%	%	[µg/m 3]	Σ pOU	%	%	[µg/m 3]	Σ pOU	%	%
Σ Aromatics	4017,4	2,36	86,6	10,2	17854,6	5,7	45,8	5,8	7280,6	1,8	66,8	11,1
Σ Alcohols	64,0	0,00	1,4	57,5	14869,6	1,7	38,2	68,2	3200,4	1,2	29,4	82,5
Σ Aldehydes	0,0	0,00	0,0	0,0	21,1	1,4	0,1	0,0	2,1	0,4	0,0	0,0
Σ Ketones	312,7	0,00	6,7	0,4	4559,7	0,2	11,7	2,4	334,4	0,0	3,1	0,8
Σ Acetates	163,9	0,00	3,5	0,2	1068,1	3,4	2,7	23,6	59,6	0,8	0,5	5,5
Σ Nitro compounds	0,0	0,00	0,0	30,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Σ Alkanes	78,4	0,00	1,7	0,0	532,0	0	1,4	0,0	16,0	0	0,1	0,0
Σ Ethers	0,0	0,00	0,0	1,5	54,9	0,0	0,1	0,0	7,5	0,0	0,1	0,0
Sums	4636,3	2,36	1,7	1,5	38960,0	12,5	1,5	0,0	10900,7	4,3	0,2	0,0
u.o./m 3	70				293,0				379			

Table IV - Ambiences analyses at work places compared with headspace paint analyses

SPECIES	PRIMER INCINERATOR							TOP AND BACKER INCINERATOR						
	INLET			Paint	OUTLET		ε	INLET			Paint	OUTLET		ε
	[µg/m3]	Σ pOU	%	%	[µg/m3]	Σ pOU	%	[µg/m3]	Σ pOU	%	%	[µg/m3]	Σ pOU	%
Σ Aromatics	49527,9	7,86	13,4	11,1	1068,6	0,05	97,9	70894,3	8,21	11,3	7,9	2026,6	0,44	99,2
Σ Alcohols	248522,7	6,37	67,4	82,5	0,0	0,00	100,0	333599,0	7,05	52,9	63,1	296,9	0,00	99,9
Σ Aldehydes	22169,6	6,23	6,0	0,0	240,8	0,54	98,9	14390,0	8,65	2,3	0,0	120,3	1,40	99,2
Σ Ketones	21580,0	2,53	5,9	0,8	1113,7	0,00	94,8	13338,9	1,91	2,1	1,4	187,5	0,00	98,6
Σ Acetates	20754,6	5,07	5,6	5,5	0,0	0,00	100,0	8777,5	4,90	1,4	12,5	21,7	0,00	99,8
Σ Nitro compounds	2830,2	0,00	0,8	0,0	782,6	0,00	-	177580,0	0,00	28,2	14,4	150,1	0,00	80,5
Σ Alkanes	294,8	0,00	0,1	0,0	5508,5	0,00	-	11515,1	0,00	1,8	0,0	31,3	0,00	99,7
Σ Ethers	2948,1	0,00	0,8	0,0	0,0	0,00	100,0	0,0	0,00	0,0	0,7	0,0	0,00	-
Sums	368627,9	28,06	0,9	0,0	8714,3	0,60	97,6	630094,7	30,72	1,8	0,7	2834,4	1,84	99,6
u.o./m 3	8444				884		89,5	19612,5				1252		93,6

Table V - Incinerators effluents analyses + abatement efficiencies compared with headspace paint analyses

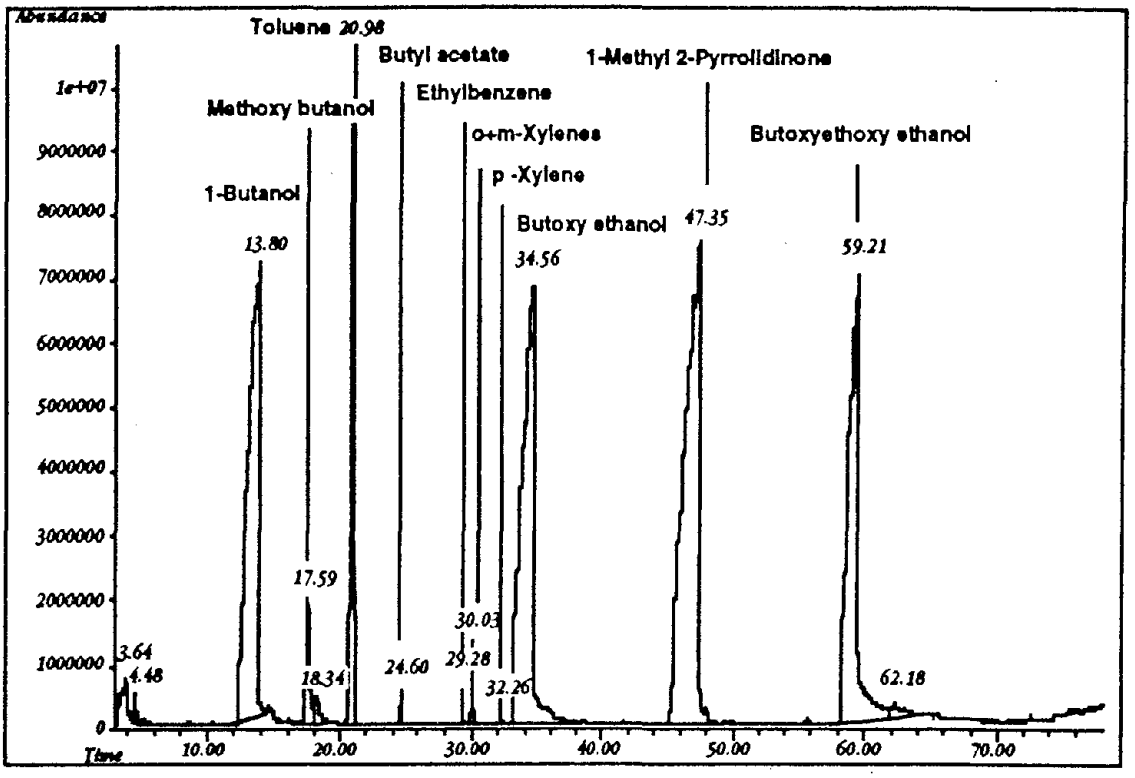


Fig. 7 - Chromatogram of back coat analysis (W-epoxy)

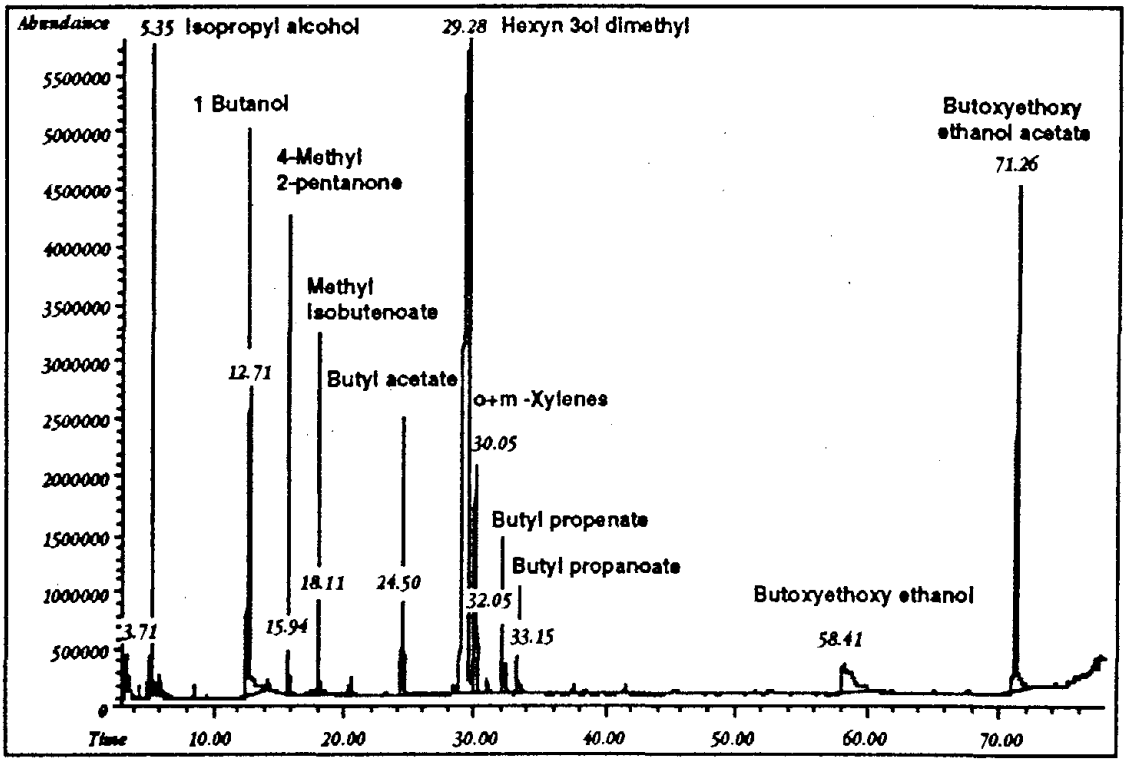
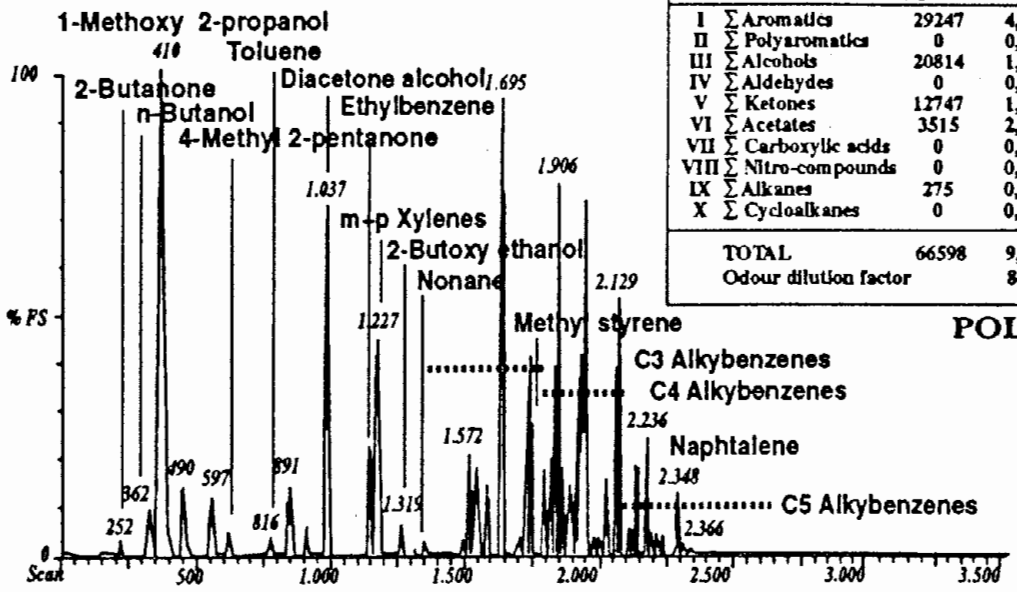


Fig. 8 - Chromatogram of top coat analysis (W-acrylic)



SPECIES		WORK PLACE [µg/Nm3]	WORK PLACE pOU	PAINT %
I	∑ Aromatics	29247	4,07	58,8
II	∑ Polyaromatics	0	0,00	0
III	∑ Alcohols	20814	1,56	39
IV	∑ Aldehydes	0	0,00	0
V	∑ Ketones	12747	1,77	0,9
VI	∑ Acetates	3515	2,01	1,2
VII	∑ Carboxylic acids	0	0,00	0
VIII	∑ Nitro-compounds	0	0,00	0
IX	∑ Alkanes	275	0,00	0,1
X	∑ Cycloalkanes	0	0,00	0
	TOTAL	66598	9,42	100,00
	Odour dilution factor		864	

POLYESTER

Fig. 9 - Chromatogram of top coat analysis (OBS)

4.2. *Discussion*

The table VI compares the levels of emissions occuring at work places during the application of a full OBS-system and a full waterborne one.

Sampling	[µg/m3]	Σ pOU (dBo)	u.o./m3
	OBS System		
Primer (EPOXY)	39718	7,36	382
Top Coat (P.E.)	30024	7,04	280
INCINERATOR inlet	637757	12,28	13083
outlet	19000	4,71	671
	W-System		
Primer (EPOXY)	7768,5	4,3*	224,5
Top Coat (P.E.)	38960	12,5	293
INCINERATOR inlet	499361,5	30,72*	14028,25
outlet	5774,5	1,84*	1068

*Maximum value

Table VI - Summary of the comparison between emissions generated by a OBS-system [7] and a W-system.

The value for the ventilation flow-rate of paint cabin corresponding to the OBS-system is the double of the flow-rate corresponding to the cabins where W-system was applied.

It can be pointed out that noticeable reductions of emissions are obtained when using W-system: the level of concentrations are equivalent even if the ventilation flow-rate is double for the OBS-system.

However major differences can be seen from work places and incinerators effluents analysis.

At work places the participation of VOC's species at the global concentration is not in accordance with the VOC's species percentage given by the headspace analysis of the paint, at the opposite of OBS-system analysis. Although alcohols are the main organic solvents in W-paints, aromatics predominates in the ambience composition, probably because the components of this latest species are not soluble in water.

So if W-system is used to reduce the ventilation air flow-rate at the work place ambiences by keeping the same level of concentration than for a OBS system, the

two systems are equivalent from a toxicity point of view. To a same level of concentration as measured in this study, W-system does not allow to reduce significantly odours concentrations.

At incinerator inlet (corresponding to the ovens outlet) and outlet, the difference consists in the presence of a greatest quantity of by-products (by partial oxidation or recombination) than for using a OBS-system. Furthermore, some by-products like nitro-compounds are not found with OBS-systems.

The first category of identified by-products are aldehydes. Aldehydes are mainly the product of the partial oxidation of the alcohols and their content into ovens and incinerators effluent outlet is obviously increased since the greatest percentage of alcohols involved in the W-paint formulation: from traces detected for OBS-system (bulk percentage ≤ 0,1 %), aldehydes concentration can reach several %. They are 100 time more odorous than alcohols and it implies greater values in dBo (odour power) but the VOC's blending effect limits very well the increasing of the odour concentration.

The second category of by-products are nitro-compounds: 2-Methyl Pyrrolidinone can be a major component of solvent phase of a W-paint. This compound is used as a reaction susceptor during curing and fully participates as a linking agent. Some quantities of this compound can however be retrieved at the incinerator inlet (0,1 % of the bulk concentration to be compared with the 30 % of the bulk composition of the organic solvents of the backer W-paint, see tables IV-VI). The thermal degradation of this component is easy but susceptible to give by-products like alkyl nitrates, nitriles and nitroalkanes. Formation of HCN is not impossible and precautions must be especially observed to maintain the incinerator temperature at a sufficient level (≥ 700 °C). No traces of nitro-compounds were found at work place ambiences.

5. Implication on the abatement techniques

They are no major disturbances to use W-system with conventional thermal incinerators but because of the presence of greater quantity of by-products precautions must be taken to keep a sufficient high temperature. Investigations led on a pilot catalytic incinerator show that no problem occurs when W-system is used.

Use of W-paints allows a deep reorientation of abatement technologies because a lot of parameters is significantly modified. Techniques such as biofiltration, adsorption, scrubbing and condensation, membrane separation can be investigated. As a matter of fact, the major identified compounds at the inlet of incinerators are ethanol (1,5-3%), n-butanal (1,3-5,1%), 1-Butanol (14,1-22,8%), toluene (6-8%) hexyn-ol-dimethyl (11 %), 2-butoxyethanol (22-29%) and 2-Pyrrolidinone 1-Methyl (0,6-28,1%). From one paint to another, the ranges of percentage (except for the latest compounds) are close. Global percentage in aromatics is included in the range 11,3-13,4%. The limited number of VOC compounds allows for recovery of solvent by adsorption or condensation. The more xenobiotic compounds for a biofiltration system are constituted by aromatics (10%); otherwise the level of concentration is not too high and a higher water content is present.

The main subsisting problem to allow such techniques is the oven temperature level. Almost all the recovery techniques needs an inlet effluent temperature reaching no more than 40 °C to be efficient. Condensation and membrane separation are the two opposite exceptions: condensation needs cryogenic temperature whereas membrane technology is promising to be used at temperature in the range of 200-250 °C.

The response at this problem is coming from new development of electrical heated ovens using magnetic induction properties [8] from which outlet effluent temperatures are liwer than 80 °C.

6. Availability

Waterborne paints are used as primer, backer and topcoat but only for building end uses, i.e. cladding, siding and roofing of industrial, commercial and residential buildings. These coatings are available only in low or semi-gloss finishes on various substrata : aluminium, hot dip galvanized steel, ...
The durability of waterborne topcoats is excellent; waterborne finishes can be classified as very high durable coatings second only to fluorocarbons.

Building market represents about the third of the coil-coating activity so W-systems can be used in large quantities.

For the full scale test done at Sollac plant, some problems about viscosity and pigments decantation into the paint barrels, emulsion at rolls application (craters formation on the surface of the coating) and vaporization rate must be solved.

7. Conclusions

The advantages and the limitations of a waterborne system in comparison with a classical based organic solvent one are well shown in this study. Full W-system allows for reducing by two the needed flow-rate both for paint cabin or area ventilation and for air dilution through the ovens and subsequently through the incinerators. Indeed, the level of odours and VOC's concentrations is lower. In such conditions it was demonstrated in a previous paper [5] that energy consumption can be kept constant or only lightly increased.

Waterborne systems are waiting for the industrial request which can spread their availability for a large range of coating. They offer new possibilities for a more environment-friendly coating operation by example by using recovery techniques for solvent reuse.

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[8] R. WANG and T. DERIAUD, *Chauffage inductif dans le traitement en continu des bandes d'acier*, Congrès européen "L'induction et ses applications industrielles", mars 1991, Strasbourg, France

CLOSING REMARKS FOR LOW- AND NO-VOC COATING TECHNOLOGIES: SECOND BIENNIAL INTERNATIONAL CONFERENCE

Michael Kosusko

First of all, I would like to thank the speakers and session chairs for contributing their time to prepare for, and/or to present their research at, what I feel has been a very productive conference. Second, I would like to thank the audience, for staying on to the very end of a long, 2½ days of exceptional presentations and for asking many excellent questions. Most of all, I would like to thank our co-sponsors at Research Triangle Institute (RTI) for their hard work and constant attention to details. RTI's Ella Darden, Coleen Northeim, and Jesse Baskir, have helped put together an excellent program and brought us all together. Finally, I wish to thank Reichhold Chemicals for sponsoring refreshments for several of our breaks.

This has been the 2nd Biennial International Conference on Low- and No-VOC Coating Technologies. The Conference had over 185 participants with 45 speakers. Overall, we have had a very diverse and exciting program featuring information on everything from powder coatings to the use of life cycle assessment for ecolabelling. The conference has provided us with the opportunity to interact with a broad range of coating researchers, suppliers, and users, with environmental advocates, and with government and trade association officials.

The overall goals of the technology development process include reduced environmental impacts, lowered process costs, and enhanced U.S. competitiveness in worldwide markets. The process of getting new, lower-emitting coating technologies developed and delivered to the user involves many players, each of whom faces unique challenges.

(1) Coating developers in industry and universities must integrate new materials and concepts from the very fundamental to the somewhat applied. Their challenge is to develop lower-emitting technologies that not only perform as well as current technologies, but perform better and at lower cost.

(2) For coatings evaluators, such as private organizations and the U.S. Environmental Protection Agency's research laboratories, the challenge is to complete thorough and objective evaluations of new technologies in terms of emissions reduction potential, performance, and cost of implementation.

(3) For technical assistance agents, such as those from state and local governments, the challenge is to keep on top of the latest technical developments, digest the information, and convey the relevant details to the user.

All of these players have been in the audience during this conference. I hope that you have had a chance to exchange information and network.

Finally, I'd like to point out that this has been an international conference and I'd like to recognize the efforts that our international colleagues have made to get here. I hope that you have enjoyed the conference and have found it to be useful and informative.

APPENDIX A

ATTENDEES LIST

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March 13-15, 1995
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